This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

LIBRARY OF THE
UNIVERSITY OF MICHIGAN

~~East Engin. Library~~
QD
1
.C52
V.92
pt. I

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

Committee of Publication:

H. E. Armstrong, Ph.D., LL.D., F.R.S.
E. C. C. Baly.
Horace T. Brown, LL.D., F.R.S.
A. W. Crossley, D.Sc., Ph.D., F.R.S.
Wyndham R. Dunstan, D.Sc., Ph.D., F.R.S.
M. O. Forster, D.Sc., Ph.D., F.R.S.
R. Meldola, F.R.S.
G. T. Morgan, D.Sc.
Sir W. Ramsay, K.C.B., LL.D., F.R.S.
A. Scott, M.A., D.Sc., F.R.S.
W. A. Tilden, D.Sc., F.R.S.
John Wade, D.Sc.

Editor:

J. C. Cain, D.Sc., Ph.D.

Sub-Editor:

A. J. Greenaway.

Assistant Sub-Editor:

C. H. Desch, D.Sc., Ph.D.

Abstractors:

E. F. Armstrong, Ph.D., D.Sc.
C. F. Baker, Ph.D., B.Sc.
G. Barger, M.A., D.Sc.
W. A. Davis, B.Sc.
H. M. Dawson, Ph.D., B.Sc.
T. Ewan, B.Sc., Ph.D.
W. H. Glover, Ph.D.
E. Goulding, B.Sc.
P. Haas, B.Sc., Ph.D.
W. D. Halliburton, M.D., F.R.S.
T. A. Henry, D.Sc.
E. Horton, B.Sc.
L. M. Jones, B.Sc.
Z. Kahan, B.Sc.
L. De Koningh.
A. McKenzie, M.A., D.Sc.
N. H. J. Miller, Ph.D.
G. T. Morgan, D.Sc.
K. J. P. Orton, M.A., Ph.D.
J. C. Philip, M.A., Ph.D.
T. H. Pope, B.Sc.
W. Robertson.
G. Senter, Ph.D., B.Sc.
W. P. Skertchly.
C. Smith, D.Sc.
L. J. Spencer, M.A.
J. J. Sudborough, Ph.D., D.Sc.
A. Jamieson Walker, Ph.D., B.A.
E. W. Wheelwright, B.A., Ph.D.
M. A. Whiteley, D.Sc.
G. Young, Ph.D.

1907. Vol. XCII. Part I.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
1907.

Richard Clay & Sons, Limited,
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

REPORT OF

THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE,
STRAND, LONDON, W.C.
13*th November*, 1907.

GENTLEMEN,

I have the honour to forward you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1908, to which I have appended, as desired by them, the names of Professors Ostwald and Urbain.

It will be seen that since our last Report a number of important re-determinations of atomic weights have been published, and the existing table in consequence reveals a number of small inconsistencies due to the original data from which the values are derived. We think it is inopportune at present to attempt to recalculate these values as the work known to be in progress on certain fundamental constants, to which reference was made in our last Report, has not yet been published. We have good reason to believe, however, that it will soon make its appearance, and we hope to be able to present an amended table with our Report for next year.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon. Secretaries,
The Chemical Society,
Burlington House,
London, W.

196011

Report of the International Committee on Atomic Weights, 1908.

Since the preparation of our report for 1907, several important determinations of atomic weights have been published. They are, briefly, as follows:

Nitrogen.—Richards and Forbes (*J. Amer. Chem. Soc.*, 1907, **29**, 808; *Zeitsch. anorg. Chem.*, 1907, **55**, 34) have re-determined the ratio between Ag and NO_3, as shown in the composition of silver nitrate. The ratio found, with all corrections applied, is $Ag : NO_3 = 100 : 57{\cdot}479$. Hence, if $Ag = 107{\cdot}930$, $N = 14{\cdot}037$, and if $N = 14{\cdot}008$, $Ag = 107{\cdot}880$. In short, the higher atomic weight hitherto assigned to silver is inconsistent with the lower value for nitrogen as found in several recent investigations.

Sulphur.—Richards and Jones (*J. Amer. Chem. Soc.*, 1907, **29**, 826; *Zeitsch. anorg. Chem.*, 1907, **55**, 72) have measured the ratio between Ag_2SO_4 and AgCl. From the data obtained, if $Ag = 107{\cdot}930$, $S = 32{\cdot}113$; a value much higher than that commonly accepted. If $Ag = 107{\cdot}880$, then $S = 32{\cdot}069$, which is near the figure given in our former tables. Additional evidence relative to this constant is much to be desired, for it influences the determination of many other atomic weights, especially those of the rare-earth metals.

Potassium.—From the ratios Ag : KCl and AgCl : KCl, Richards and Staehler (*J. Amer. Chem. Soc.*, 1907, **29**, 623; *Ber.*, 1906, **39**, 3611) find $K = 39{\cdot}114$, when $Ag = 107{\cdot}930$ and $Cl = 35{\cdot}473$. From the corresponding bromide ratios, with $Br = 79{\cdot}953$, Richards and Mueller (*J. Amer. Chem. Soc.*, 1907, **29**, 639; *Zeitsch. anorg. Chem.*, 1907, **53**, 423) find $K = 39{\cdot}1143$ and $39{\cdot}1135$. The final result of both researches is $K = 39{\cdot}114$, a distinct lowering of the constant in question.

Manganese.—Atomic weight re-determined by Baxter and Hines (*J. Amer. Chem. Soc.*, 1906, **28**, 1560; *Zeitsch. anorg. Chem.*, 1906, **51**, 202) from analyses of the chloride and bromide. The mean of their very concordant determinations is $Mn = 54{\cdot}957$, when $Ag = 107{\cdot}930$.

Cobalt.—From new analyses of the chloride, Baxter and Coffin (*J. Amer. Chem. Soc.*, 1906, **28**, 1580; *Zeitsch. anorg. Chem.*, 1906, **51**, 171) find $Co = 58{\cdot}997$, or 59 in round numbers. This confirms the earlier determinations by Richards and Baxter.

Indium.—Mathers (*J. Amer. Chem. Soc.*, 1907, **29**, 485; *Ber.*, 1907, **40**, 1220), from analyses of indium chloride, found $In = 114{\cdot}88$. From the bromide, $In = 114{\cdot}86$. The author recommends the adoption of the rounded-off value, 114·9, when $Ag = 107{\cdot}93$, $Cl = 35{\cdot}473$, and $Br = 79{\cdot}953$.

Tellurium.—Norris (*J. Amer. Chem. Soc.*, 1906, **28**, 1675), by twelve concordant reductions of the basic nitrate, $2TeO_2 \cdot HNO_3$ to TeO_2, found the atomic weight of tellurium to be 127·48, when N = 14·01. With N = 14·04, Te = 127·64, which is in better agreement with other recent determinations. The true cause of the difference is not clear.

Neodymium.—Holmberg (*Zeitsch. anorg. Chem.*, 1907, **53**, 83) has re-determined the atomic weight of this element by synthesis of the sulphate from the oxide. In mean, when S = 32·06, Nd = 144·08. This is higher by 0·48 than the value given in our table.

Dysprosium.—In two series of determinations, based upon the ignition to oxide of the octohydrated sulphate, Urbain and Demenitroux (*Compt. rend.*, 1906, **143**, 598) find for the atomic weight of dysprosium values ranging between 162·29 and 162·75. In mean, Dy = 162·53.

Radium.—In a new series of three determinations, made on about 4 decigrams of the carefully-purified chloride, Madame Curie (*Compt. rend.*, 1907, **145**, 422) has found Ra = 226·18, when Ag = 107·8 and Cl = 35·4. With Ag = 107·93 and Cl = 35·45, Ra = 226·45. This is more than a unit above her previous measurements.

From the data here given, and from those cited in previous reports, it is evident that the entire table of atomic weights is in need of revision. The values assigned to K and Na are too high; those given to Cl and S are too low, and these constants affect the determinations of many others. They depend, however, upon the atomic weight of silver, which is probably, but not certainly, as low as 107·88. It is well known that work upon these fundamental constants is now nearing completion in several laboratories, notably under T. W. Richards, W. A. Noyes, and probably other investigators also. Within a few months, it should be possible to enter upon a satisfactory revision of the table, a task which would be unsatisfactory if undertaken now. It is true, as Brauner has suggested, that the present table contains inconsistencies, but they are small in amount, and are due to inconsistencies in the original data from which the values are derived. In our next report, we hope to recompute the entire table; but meanwhile, awaiting the completion of the researches which we know to be in progress, we prefer to leave the table practically unchanged. A conservative policy seems to be safer than one of haste, and the delay of another year will do no harm. One exception to the rule may, however, be made. Dysprosium, with the atomic weight 162·5, may now be properly added to the list of the chemical elements, and we recommend its insertion in the table.

It is with the deepest regret that we record the loss, by death, in February last, of our distinguished colleague, Prof. Moissan. The Chemical Society of Paris has designated Monsieur G. Urbain as his successor upon this Committee.

(Signed) F. W. Clarke,
W. Ostwald,
T. E. Thorpe,
G. Urbain.

1908.

International Atomic Weights.

		O=16.			O=16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	143·6
Argon	A	39·9	Neon	Ne	20
Arsenic	As	75·0	Nickel	Ni	58·7
Barium	Ba	137·4	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	191
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·96	Palladium	Pd	106·5
Cadmium	Cd	112·4	Phosphorus	P	31·0
Cæsium	Cs	132·9	Platinum	Pt	194·8
Calcium	Ca	40·1	Potassium	K	39·15
Carbon	C	12·00	Praseodymium	Pr	140·5
Cerium	Ce	140·25	Radium	Rd	225
Chlorine	Cl	35·45	Rhodium	Rh	103·0
Chromium	Cr	52·1	Rubidium	Rb	85·5
Cobalt	Co	59·0	Ruthenium	Ru	101·7
Columbium	Cb	94	Samarium	Sa	150·3
Copper	Cu	63·6	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	166	Silicon	Si	28·4
Europium	Eu	152	Silver	Ag	107·93
Fluorine	F	19·0	Sodium	Na	23·05
Gadolinium	Gd	156	Strontium	Sr	87·6
Gallium	Ga	70	Sulphur	S	32·06
Germanium	Ge	72·5	Tantalum	Ta	181
Glucinum	Gl	9·1	Tellurium	Te	127·6
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·0	Thallium	Tl	204·1
Hydrogen	H	1·008	Thorium	Th	232·5
Indium	In	115	Thulium	Tm	171
Iodine	I	126·97	Tin	Sn	119·0
Iridium	Ir	193·0	Titanium	Ti	48·1
Iron	Fe	55·9	Tungsten	W	184
Krypton	Kr	81·8	Uranium	U	238·5
Lanthanum	La	138·9	Vanadium	V	51·2
Lead	Pb	206·9	Xenon	Xe	128
Lithium	Li	7·03	Ytterbium	Yb	173·0
Magnesium	Mg	24·36	Yttrium	Yt	89·0
Manganese	Mn	55·0	Zinc	Zn	65·4
Mercury	Hg	200·0	Zirconium	Zr	90·6

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.
6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.
7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride*, *potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

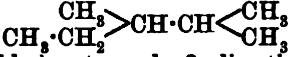
11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

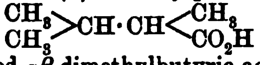
14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ α-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,



$$\begin{matrix}CH_3\\CH_3\cdot CH_2\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

or $CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$ should be termed βγ-dimethylpentane, not methylethyl*iso*propylmethane, and



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CO_2H\end{matrix}$$

or $CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$ should be termed αβ-dimethylbutyric acid, not αββ-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt\cdot CHMe\cdot CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3\cdot CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc\cdot CHMe\cdot CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2\cdot CO_2H$, and not $C_6H_3(OEt)_2\cdot CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2\cdot CO_2H$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, β-anilino-acrylic acid, $NHPh\cdot CH{:}CH\cdot CO_2H$, α-iminopropionic acid, $NH{:}CMe\cdot CO_2H$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 3rd decade (1893–1902) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^α for $CH_2 \cdot CH_2 \cdot CH_3$, Pr^β for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO \cdot CH_3$, and Bz for $CO \cdot C_6H_5$.

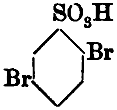
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

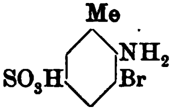
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

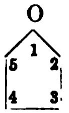


is 2 : 5-dibromobenzenesulphonic acid;

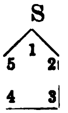


is 3-bromo-*o*-toluidine-5 sulphonic acid.

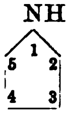
29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (2nd edition, 1899, pp. 16—26) should be used, of which the following schemes may be regarded as typical :—



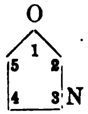
Furan.



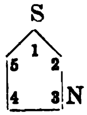
Thiophen.



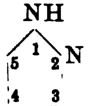
Pyrrole.



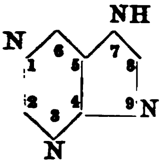
Oxazole.



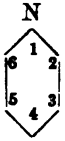
Thiazole.



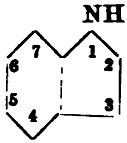
Pyrazole.



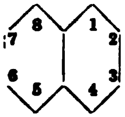
Purine.*



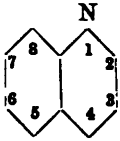
Pyridine.



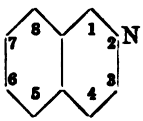
Indole.



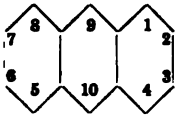
Naphthalene.



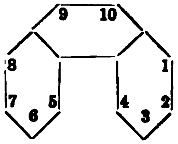
Quinoline.



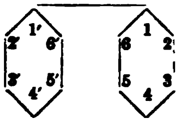
*iso*Quinoline.



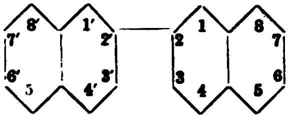
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulæ and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

⁂ The Editor's decision, in all matters connected with the Abstracts, must be considered final.

---

[*] This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path.	Beiträge für chemische Physiologie und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Bio-chem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.*	Chemisches Zentralblatt.

* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Geol.	Journal of Geology.
J. Hygiene.	Journal of Hygiene.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Lancet.	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie	Metallurgie.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch.	Pharmaceutical Archives.
Pharm. Centr-h.	Pharmazeutische Centralhalle.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsh. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Farb. Ind.	Zeitschrift für Farben-Industrie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photograph. Photophysik. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

Officers and Council.

Elected March 22, 1907.

PRESIDENT.

SIR WILLIAM RAMSAY, K.C.B., LL.D., F.R.S.

VICE-PRESIDENTS

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

H. E. ARMSTRONG, Ph.D., LL.D., F.R.S.
A. CRUM BROWN, D.Sc., LL.D., F.R.S.
SIR WILLIAM CROOKES, D.Sc., F.R.S.
SIR JAMES DEWAR, M.A., LL.D., F.R.S.
A. G. VERNON HARCOURT, D.C.L., F.R.S.
RAPHAEL MELDOLA, F.R.S.
HUGO MÜLLER, Ph.D., LL.D., F.R.S.
W. ODLING, M.A., M.B., F.R.S.
J. EMERSON REYNOLDS, Sc.D., F.R.S.
SIR HENRY E. ROSCOE, LL.D., F.R.S.
W. J. RUSSELL, Ph.D., F.R.S.
T. E. THORPE, C.B., LL.D., F.R.S.
W. A. TILDEN, D.Sc., F.R.S.

VICE-PRESIDENTS.

J. J. DOBBIE, M.A., D.Sc., F.R.S.
RUDOLPH MESSEL, Ph.D.
SIR ALEXANDER PEDLER, C.I.E., F.R.S.
W. H. PERKIN, Ph.D., F.R.S.
A. SMITHELLS, B.Sc., F.R.S.
W. P. WYNNE, D.Sc., F.R.S.

TREASURER.

ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

SECRETARIES.

M. O. FORSTER, D.Sc., Ph.D., F.R.S.
A. W. CROSSLEY, D.Sc., Ph.D., F.R.S.

FOREIGN SECRETARY.

HORACE T. BROWN, LL.D., F.R.S.

OTHER MEMBERS OF THE COUNCIL.

E. C. C. BALY.
G. T. BEILBY, F.R.S.
BERNARD DYER, D.Sc.
W. R. E. HODGKINSON, Ph.D.
E. GRANT HOOPER.
H. A. D. JOWETT, D.Sc.
H. R. LE SUEUR, D.Sc.
F. E. MATTHEWS, Ph.D.
G. T. MOODY, D.Sc.
A. G. PERKIN, F.R.S.
W. J. SELL, M.A., D.Sc., F.R.S.
JOHN WADE, D.Sc.

ASSISTANT SECRETARY.

S. E. CARR.

LIBRARIAN.

F. W. CLIFFORD.

IMPORTANT NOTICES.

NOTICES TO AUTHORS OF PAPERS.

All communications for the Journal and for the **Proceedings** of the Society should be addressed to **"The Secretaries, Chemical Society, Burlington House, W."**

The attention of authors is directed to the following resolutions of the Council.

"No communication shall be included in the list of titles of papers to be brought before a Meeting of the Society, unless it is in the hands of the Secretaries **at least three days** before the date of the Meeting; and no announcement of titles can be made in the Proceedings until the communications have been received by the Secretaries."

"Papers which, on the report of referees, are deemed by the Council unsuitable for publication in the Transactions, shall be deposited in the Society's Archives." Authors are therefore advised to retain copies of their papers.

In all cases, an abstract of the paper, not exceeding three hundred words in length, should be supplied for insertion in the Proceedings. Communications are put down on the list for reading in the order in which they are received.

Authors are requested to write on their papers and abstracts **the address to which they wish proofs to be sent**, also to send their corrected proofs without delay to the Editor, **28, Pembury Road, Clapton, N.E.**, *and not to the Printers*. If authors require more than the **50 copies** allowed by the Society, they should inform the Editor at the time they send in their corrected proofs, when the extra copies will be supplied at cost price.

It has been resolved by the Council that communications made to the Society which have **already appeared in any Foreign Journal** shall not be published in the Society's Transactions, unless this course is **specially recommended** by the Publication Committee, and this recommendation approved by the Council.

ILLUSTRATIONS, AND PLATES OF CURVES.

As the **Illustrations** for the Journal (including curves) are, as far as possible, executed in photographic "process" work, the drawings, &c., accompanying the papers **must be drawn carefully on a scale about twice the size of the finished block, on smooth white Bristol board in Indian ink, so as to admit of the blocks being prepared directly from the drawings.** Any lettering on these drawings should be of such a size that it will be clearly legible when reduced.

When it is necessary to employ **Plates**, these must be also of convenient dimensions.

Information as to **Illustrations** and the dimensions of **Plates** can be obtained on application to the Editor.

Abstractors are requested to send their MSS. and corrected proofs to the **Sub-editor**, The Orchard, Chertsey, Surrey, and to communicate change of address to the **Printers** (Messrs. Richard Clay and Sons, Limited, 8, Bread Street Hill, E.C.), as well as to the **Editors**.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Action of Nitric Acid on Saturated Hydrocarbons. Nitration of Saturated Hydrocarbons containing two *iso*Propyl Groups. XIV. & XV. Michael I. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 109—123, 124—141. Compare Abstr., 1905, i, 764).—βε-Dimethylhexane is best obtained from β-methylpropyl bromide. When treated with nitric acid, the substances formed depend on: (1) the temperature; (2) whether the experiment is carried out in sealed tubes or in open vessels; (3) the sp. gr. of the nitric acid employed; (4) the duration of heating.

The mononitro-βε-dimethylhexanes.—Under the most favourable conditions 83°/₀ of the β-nitro-compound and 17°/₀ of a mixture of the α- and γ-derivatives were obtained. β-Nitro-βε-dimethylhexane, $NO_2 \cdot CMe_2 \cdot [CH_2]_2 \cdot CHMe_2$, is a colourless liquid, b. p. 200—201°/760 mm., D_0^0 0·9396, D_0^{20} 0·9205, n_D^{15} 1·43055. In an ethereal or benzene solution, sodium reacts violently with it, forming a characteristic metallic compound (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, ii, 234 ; 1902, **34**, ii, 45). The corresponding amine, formed by reduction with tin and hydrochloric acid, b. p. about 744°(74·4°?)/749 mm., D_0^0 0·7803, $D_0^{22·3}$ 0·7605 (in *Ber.*, 1895, **28**, 1854, the same author gives b. p. 145°/746·5 mm., $n_D^{24·3}$ 1·41655). The hydrochloride, m. p. 157—160°, the platinichloride, $(C_8H_{17}NH_2)_2,H_2PtCl_6$, and the normal *sulphate*, m. p. about 235°, are described. α-*Nitro-βε-dimethylhexane*,

$$NO_2 \cdot CH_2 \cdot CHMe \cdot [CH_2]_2 \cdot CHMe_2,$$

b. p. 100—105°/20 mm. The γ-*nitro*-compound,

$$CHMe_2·CH(NO_2)·CH_2·CHMe_2,$$

forms a *bromo*-compound, $CHMe_2·CBr(NO_2)·CH_2·CHMe_2$, D^0_0 1·3211, D^{20}_0 1·3033, and n^{20}_D 1·47857. *βε-Dinitro-βε-dimethylhexane*,

$$NO_2·CMe_2·[CH_2]_2·CMe_2·NO_2,$$

crystallises from benzene in colourless, odourless scales resembling naphthalene, m. p. 124—125°, distils and decomposes under ordinary pressure. The formula is deduced: (1) from its insolubility in alkalis; (2) its formation from the corresponding β-mononitro-compound. Zinc dust and acetic acid, but not tin and hydrochloric acid, readily reduce it to the corresponding amine, a colourless liquid, b. p. 186°/753 mm., D^0_0 0·8580, $D^{14·5}_0$ 0·8485, and $n^{14·5}_D$ 1·45062. The following salts all decompose at their melting points: the *hydrochloride* and *hydrobromide*, above 300°; the *nitrate*, at 226°; the *picrate*, at 293°; the *oxalate*, at 269—270°; and the *auribromide*, at 295—300°. The platinichloride,

$$C_8H_{16}(NH_2)_2,H_2PtCl_6,$$

and the *dibenzoyl* derivative, $C_8H_{16}(NHBz)_2$, m. p. 215°, were obtained.

βζ-Dimethylheptane, $CHMe_2·[CH_2]_3·CHMe_2$, b. p. 134—135°/747 mm., D^0_0 0·7265, D^{16}_0 0·7144, and n^{16}_D 1·40270 (compare Wurtz, *Jahresber.*, 1855, 575). It is conveniently nitrated at 120°, using nitric acid D 1·075, the chief product of the reaction being the β-*mononitro*-derivative, $NO_2·CMe_2·[CH_2]_3·CHMe_2$, b. p. 113—115°/25 mm., D^0_0 0·9281, D^{18}_0 0·9150, and n^{18}_D 1·43256. Tin and hydrochloric acid reduce the nitro-compound, forming *β-amino-βζ-dimethylheptane*, b. p. 165·5—166·5°/754 mm., D^0_0 0·7660, D^{20}_0 0·7533, and n_D 1·42455. The *hydrochloride*, *nitrate*, *sulphate*, and *picrate* are all well-defined, crystalline salts. The *platinichloride*, $(C_9H_{19}NH_2)_2,H_2PtCl_6$, blackens at 200° and does not melt below 255°. *βζ-Dinitro-βζ-dimethylheptane*,

$$NO_2·CMe_2·[CH_2]_3·CMe_2·NO_2,$$

crystallises in flat needles, m. p. 74—74·5°, and cannot be distilled unchanged. Zinc dust and acetic acid reduce it to *βζ-diamino-βζ-dimethylheptane*, which does not solidify at −15°, and has b. p. 204—206°/749 mm., D^0_0 0·8544, $D^{24·5}_0$ 0·8388, and $n^{24·5}_D$ 1·4481. The *hydrochloride* does not melt even at 241°, but darkens at 195°. The *dibenzoyl* derivative, $C_9H_{18}(NH·COPh)_2$, m. p. 159—160°, distils without decomposition, but in the presence of ammonium chloride a new *substance* is formed.

βη-Dimethyloctane, $CHMe_2·[CH_2]_4·CHMe_2$, can be nitrated both in closed and open vessels. The products obtained and the progress of the reaction depend on the same circumstances as in the case of the heptane hydrocarbon. When concentrated nitric acid is employed, vigorous oxidation is also noticeable. The process of nitration is greatly facilitated by the removal of the nitro-compounds as formed, and also by the use of nitric acid which has been used in previous experiments. Mercuric nitrate yields no nitro-derivatives when the experiment is performed in an open vessel, whilst aluminium and bismuth nitrates give chiefly α- and γ-nitro-derivatives. In a sealed tube, aluminium nitrate reacts vigorously only when dry. An attempt to find a sharper reaction than Meyer's for identifying and separating α- and γ-nitro-derivatives has not led to any conclusive results so far.

α-Nitro-βη-dimethyloctane, $NO_2·CH_2·CHMe·[CH_2]_4·CHMe_2$, is often obtained almost pure by nitrating the hydrocarbon with concentrated nitric acid; b. p. 125—127°/17 mm., or 235—237°/760 mm., then decomposing; D_0^0 0·94176, D_0^{21} 0·9246, and n_D^{21} 1·4426. Tin and hydrochloric acid reduce it, giving the corresponding *amine* and the *aldehyde*, $CHMe_2\cdot[CH_2]_4\cdot CHMe\cdot CHO_2$, which is also formed by the action of concentrated nitric acid on $\beta\eta$-dimethyloctane; it has b. p. 184·5—185°/744 mm., D_0^0 0·8356, D_0^{20} 0·8204. γ-(or δ)Nitro-$\beta\eta$-dimethyloctane, obtained by treating the hydrocarbon with nitric acid, D 1·075, has b. p. 129—132°, D_0^{20} 0·9115. On reduction with tin and hydrochloric acid, it yields the corresponding amine, b. p. 190—192°, D_0^{20} 0·7934; a small quantity of a *ketone*, b. p. 190—192°, is also formed. β-Nitro-$\beta\eta$-dimethyloctane is a colourless liquid solidifying in a mixture of solid carbon dioxide and ether, b. p. 125°/22·5 mm., or 135—137°/749 mm., when it decomposes; D_4^{20} 0·9092, n_D^{20} 1·43570. It is reduced by tin and hydrochloric acid to the corresponding amine, b. p. 190°/758 mm., D_0^{20} 0·7815, and n_D 1·42793. With sodium, the β-nitro-derivative reacts violently, forming a characteristic *sodium* derivative. $\beta\eta$-Dinitro-$\beta\eta$-dimethyloctane, m. p. 101·5—102°; the heat of combustion is 1513·614 Cal. per gram mol. When its ethereal solution is heated with sodium in a sealed tube, a mixture of hydrocarbons is obtained, b. p. 165—170°, and having a composition which lies between $C_{10}H_{20}$ and $C_{10}H_{18}$. These hydrocarbons are either similar to or identical with the substances obtained from the dry distillation of the hydrochloride of the diamine, $C_{10}H_{20}(NH_2)_2$. Zinc dust and acetic acid reduce the dinitro-derivative forming the corresponding diamine which forms crystals, m. p. 31°, b. p. 228·5°/747 mm., D_0^{28} 0·8344, and n_D^{28} 1·4485. When exposed to air it absorbs carbon dioxide, forming a solid salt. The hydrochloride, m. p. 168—170°, the *hydrobromide*, m. p. 265°, the sulphate, m. p. above 300°, the *oxalate*, m. p. 292·5—293°, the *picrate*, m. p. 255—256°, and the *auribromide*, m. p. 220—222°, all decompose at their melting point. The platinichloride, $C_{10}H_{20}(NH_2)_2,H_2PtCl_6$, forms shiny, orange-yellow, prismatic crystals. The *benzoyl* derivative, $C_{10}H_{20}(NHBz)_2$, m. p. 206·5—207°. Z. K.

Constitution of the Acetylidene Compounds. JAMES W. LAWRIE (*Amer. Chem. J.*, 1906, **36**, 487—510).—An extension of Nef's views (Abstr., 1898, i, 105, 114) as to the halogen-substituted derivatives of acetylene. The author considers that it is now proved that all the known mono- and di-halogen derivatives of acetylene belong to the acetylidene series, whilst the existence of corresponding compounds with the acetylene constitution is considered improbable.

When well-cooled dibromoacetylidene is added to aqueous hydriodic acid, D 1·96, combination takes place with formation of dibromoiodoethylene together with some dibromodi-iodoethylene. *Dibromoiodoethylene*, $CBr_2{:}CHI$, is a sweet smelling oil, b. p. 91°/15 mm., D^{24} 2·952. The constitution of this substance was ascertained by the following experiments. When dibromoiodoethylene is treated with fuming nitric acid at −10°, it is converted into dibromoacetic acid and iodine. Tribromoethylene undergoes a similar oxidation. The formation of dibromoacetic acid in these reactions is explained as follows. The dibromoiodoethylene or tribromoethylene is dissociated into hydrogen iodide or bromide and dibromoacetylidene, $CBr_2\colon C$; the latter compound is oxidised to dibromoacetylidene oxide, $CBr_2\colon CO$, and this absorbs water with production of dibromoacetic acid. In confirmation of this, it has been observed that tribromo- and tetrabromoethylene unite directly with oxygen at 50° with formation of dibromo- and tribromo-acetyl bromides respectively.

When dry oxygen is passed through a mixture of dibromoacetylidene and alcohol, carbon monoxide is evolved and tetrabromoethylene, oxalic acid, and dibromoacetic acid are produced. The reactions which take place are as follows: (1) the main reaction (78·4%), $2C_2Br_2 + O_2 = C_2Br_4 + 2CO$ (including some CO_2); (2) (15·54%), $C_2Br_2 + O_2 = COBr\cdot COBr$; and (3) (6·06 %),

$$2C_2Br_2 + O_2 + 2EtOH = 2CHBr_2\cdot CO_2Et.$$

When dibromoiodoethylene or tribromoethylene is treated with alcoholic sodium phenoxide, a large yield of phenyl dibromovinyl ether, $CBr_2\colon CH\cdot OPh$, is obtained, D^{25} 1·799. If this ether is treated with fuming nitric acid at −10°, it is converted into a mixture of isomeric dinitrophenyl dibromoacetates, $CHBr_2\cdot CO_2\cdot C_6H_3(NO_2)_2$. It is evident, therefore, that in dibromoacetylidene both the bromine atoms are attached to the same carbon atom. Further, since the dibromoiodoethylene obtained by the action of iodine on dibromoacetylidene (Lemoult, Abstr., 1903, i, 596) is identical with that obtained by Nef (Abstr., 1898, i, 114) by the action of bromine on di-iodoacetylidene, it follows that di-iodoacetylidene must have the constitution $CI_2\colon C$.

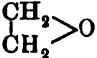
When phenyl dibromovinyl ether is heated at 100° in presence of alcohol, water, or acetic acid, it loses hydrogen bromide and is converted into phenol and bromoacetic acid or its ester. E. G.

Bromine as a Differential Reagent for Isomeric Secondary and Tertiary Aliphatic Alcohols. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 424—435).—The action of bromine on the secondary and tertiary aliphatic alcohols containing from four to nine atoms of carbon has been investigated, and it is shown that the replacement by bromine of hydrogen attached to the carbon united to the hydroxyl group or, in the case of tertiary alcohols, the hydrogen attached to the carbon contiguous to this, takes place the less readily the more hydrogenated these groups are.

In general the secondary alcohols react energetically and even almost explosively with bromine at the ordinary temperature, and an intermediate compound appears to be formed, hydrogen bromide being evolved only at the end of the reaction. The tertiary alcohols, on the contrary, do not react immediately with bromine in the cold even on exposure to sunlight, but action takes place rapidly in most cases on warming, hydrogen bromide being evolved, however, only at the end of the reaction. The changes observed on the addition of bromine to a number of these alcohols are described in detail in the original, and it is pointed out that the tertiary alcohols do not all begin to react with bromine at the same temperature, and, similarly, when the reaction is carried out in the cold, the periods of time which elapse before action commences also differ. It is considered that bromine, like oxalic and hydrochloric acids and acetyl chloride, may be used in the way indicated to distinguish between secondary and tertiary aliphatic alcohols, but it is only applicable in the cases of simple alcohols in which the alcoholic function is not modified by the previous introduction of other radicles. T. A. H.

Catalytic Reactions at High Temperatures and Pressures. X. Influence of Pressure. WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 63—75. Compare Abstr., 1904, ii, 645).—At high pressures, the catalytic decomposition of alcohol with alumina as catalyst is considerably diminished, as shown (1) by the slowness of the reaction, (2) by its remaining at the first stage, for example, $2EtOH \rightleftarrows OEt_2 + H_2O$. The apparatus previously employed has now been so modified that any quantity of gas can be forced into the reaction tube and its pressure determined, after which the tube can be disconnected from the gas supply and heated. At temperatures above 450° and pressures near to 26 atmos., hydrogen in presence of iron reduces the decomposition products of aldehyde, forming saturated hydrocarbons, but neither carbon dioxide up to 50 nor nitrogen up to 78 atmos. pressure has any influence on the course of the catalytic decomposition of alcohol. When the experiments were performed in iron tubes, the residual liquid contained undecomposed alcohol, aldehyde, and higher unsaturated hydrocarbons, C_nH_{2n}, formed by the polymerisation of ethylene. Ethylene very readily polymerises when heated in a sealed tube at 400—450° in the presence of iron or copper, but at very high temperatures much ethane, methane, and hydrogen are also obtained as by-products. In the presence of an excess of hydrogen more gaseous hydrocarbons, chiefly methane, are obtained. The reaction always tends to an equilibrium, after which further heating no longer produces any change in pressure or in the proportion of the substances formed. In the presence of reduced nickel as catalyst, ethane and methane are produced. Time and pressure curves are given for the polymerisation of ethylene at various temperatures, from which it is observed that $(dp/dt)_{\max.}$ varies considerably between 400° and 450°. Z. K.

Catalytic Reactions at High Temperatures and Pressures. XI. Reducing Catalysts. WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 75—92. Compare preceding abstract).—In order to arrive at an explanation of the catalytic decomposition of the alcohols, it is possible either to heat alcohols with catalysts in sealed tubes, or to allow aldehydes or ketones to react with hydrogen in presence of catalysts. When acetaldehyde was heated with dry hydrogen in the presence of iron at 400—450° under 60 atmos. pressure, no variation in pressure occurred and only the ordinary products of its decomposition were obtained. When acetone was heated in a similar manner at 400° and 107 atmos. pressure, the pressure steadily diminished, but equilibrium was reached after sixteen hours. The gaseous products obtained were small quantities of olefines and carbon dioxide, 80% of hydrogen, and 16% of paraffins, whilst the liquid products were probably olefines and some *iso*propyl alcohol, Similar experiments and at various temperatures and pressures were performed, using reduced nickel as catalyst (*Compt. rend.*, 1903–4–5), and time-pressure curves are drawn for acetone, methyl ethyl ketone, benzaldehyde, and camphor. Under high pressures and with excess of hydrogen, ketones are converted quantitatively into secondary alcohols. Aromatic aldehydes are reduced first to aromatic and finally to polymethylene hydrocarbons. Fatty alcohols and also ethyl ether do not decompose below 300°. The reducing action is slow and reached a maximum, aldehydes and saturated hydrocarbons being produced. If hydrogen is not previously introduced, carbon monoxide is also formed. No olefines are produced in either case, since reduced nickel causes the change $C_2H_4 \longrightarrow C_2H_6$ to take place even at low temperatures. Experiments on benzene derivatives show that the benzene nucleus is not hydrogenated even at very high pressure (220 atmos.) and temperatures in presence of copper, aluminium, or iron. In the presence of reduced nickel the reduction of the nucleus proceeds slowly, *dp/dt* never reaching a very high value, and side chains containing oxygen in whatever form are completely reduced, thus $COPh{\cdot}CHPh{\cdot}OH \longrightarrow CH_2Ph{\cdot}CH_2Ph$. Benzene is converted quantitatively into *cyclo*hexane, whilst phenol probably yields hexanone at low temperatures and hydroxy*cyclo*hexane at high ones. Quinol is slowly converted into 1 : 4-dihydroxy*cyclo*hexane, but if the temperature exceeds 300°, the ring is destroyed and methane is the main product. Hexamethylene, when heated in an iron tube under ordinary, or under 150 atmos., pressure, gave benzene, hydrogen, and gaseous paraffins and olefines, whilst hydroxy*cyclo*hexane and menthol are converted into cyclic ketones. Z. K.

Catalytic Reactions at High Temperatures and Pressures. XII. Dehydration under the Influence of Alumina. WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 92—97. Compare preceding abstract).—When *iso*amyl ether or alcohol is passed through a copper tube containing powdered alumina at 400—450°, the isomeric amylenes and water are produced; the same reaction takes place under high pressures, but in seven hours the pressure reaches a maximum and the reaction becomes reversible. The introduction of considerable quantities of water has no effect on the course of the reaction. When the vapour of acetaldehyde is passed through a copper tube containing alumina at 420—480°, a liquid is obtained consisting chiefly of acetaldehyde and paracetaldehyde, but no gases; *iso*butaldehyde behaves similarly. When ethylene glycol is heated under ordinary or high pressure, its dehydration proceeds very quickly and is complete in an hour. No gases are formed, the product of the reaction being water, acetaldehyde, and paracetaldehyde, and also small quantities of crotonaldehyde, according to the equation $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OH - H_2O =$  $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!>O \longrightarrow CH_3{\cdot}CHO \longrightarrow (C_2H_4O)_2$, whilst crotonaldehyde is probably formed from aldol which is yielded by acetaldehyde. When heated at 300—320°, pinacone undergoes the following reaction: $OH{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH = CMe_3{\cdot}COMe + H_2O$. Cyclic alcohols, such as menthol, borneol, and hydroxy*cyclo*hexane, under similar conditions lose water and yield unsaturated cyclic hydrocarbons. Z. K.

Addition of Hypochlorous Acid to Ethylene Compounds. Louis Henry (*Bull. Acad. roy. Belg.*, 1906, 523—557).—A critical *résumé* is given of the work done since 1862 by the author on the nature of the chlorohydrins formed by the addition of hypochlorous acid to propylene, *iso*butylene, and amylene, and the bearing of the results of other investigators on this. The view previously mentioned (Abstr., 1902, i, 417; 1903, i, 2, 725), that with propylene a mixture of α-chloro*iso*propyl and β-chloropropyl alcohols is formed, is extended to *iso*butylene and amylene, and it is suggested that in each of these cases the product formed on the addition of hypochlorous acid consists of a mixture of the two possible isomeric chloro-alcohols. The principal papers referred to are Henry, Abstr., 1874, i, 679, 978; 1875, i, 443; 1876, ii, 284, 620; Markownikoff, Abstr., 1876, i, 338; Michael, 1900, i, 321, [with Leighton] 1906, i, 551, 781, and Krassusky, Abstr., 1901, i, 246. T. A. H.

[Addition of Hydrogen Chloride to *iso*Butylene Oxide]. Louis Henry (*Ber.*, 1906, **39**, 3677—3679).—Polemical, a reply to Michael, Abstr., 1906, i, 781. A. McK.

Cycles of Reactions which Determine Isomerisation. Maurice Delacre (*Bull. Soc. chim.*, 1906, [iii], **35**, 1088—1092. Compare Abstr., 1906, i, 477, 518, 551, 784).—The isomerisation of substances brought about by the action of external agents such as alkalis is of two kinds, irreversible (true molecular transposition) and reversible. If pinacolin may be represented by a single formula, the following cycles of reactions in which two inverse isomerisations occur may be regarded as established: (1) $OH{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH \longrightarrow CMe_3{\cdot}COMe \longrightarrow CMe_3{\cdot}CHMe{\cdot}OH \longrightarrow CMe_2{:}CMe_2 \longrightarrow OH{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH$. (2) $CMe_3{\cdot}CH{:}CH_2 \longrightarrow CMe_2{:}CMe_2 \longrightarrow CMe_2Br{\cdot}CMe_2Br \longrightarrow CMe_3{\cdot}COMe \longrightarrow CMe_3{\cdot}CCl{:}CH_2 \longrightarrow CMe_3{\cdot}CH{:}CH_2$. In addition, therefore, to the well-authenticated cases of unsymmetrical isomerisation, there must now be recognised cases in which the reverse action takes place almost quantitatively, although it is possible that these are the result of the peculiar structure of pinacolin. T. A. H.

Friedel's Pinacolyl Acetate. Maurice Delacre (*Bull. Soc. chim.*, 1906, [iii], **35**, 1093—1094).—The iodide obtained by saturating tetramethylethylene ($\beta\gamma$-dimethyl-Δ^{β}-butylene) with hydrogen iodide, when warmed with silver acetate and then distilled, regenerates the original hydrocarbon. Similarly, the iodide obtained by treating pinacolyl alcohol with hydriodic acid at 110°, when treated with silver acetate, does not furnish pinacolyl acetate. The author is therefore unable to confirm Friedel's statements on these points (*Dict. chim., Wurtz*, II, 1025; compare Henry, Abstr., 1906, i, 329, and Delacre, *ibid.*, i, 551). If the production of the acetate from the iodide is eventually realised, it must be assumed that in the above experiments the author has, by working under conditions differing from those observed by Friedel, induced initially the change of the iodide $CMe_3 \cdot CHMeI$ into $CHMe_2 \cdot CMe_2I$. T. A. H.

Ethyl Propenyl Ether. ALEXEI E. TSCHITSCHIBABIN (*J. pr. Chem.*, 1906, [ii], **74**, 423—424. Compare Abstr., 1906, i, 397).—Ethyl propenyl ether is obtained in a 70 to 80% yield by the slow distillation of β-ethoxymethylacrylic acid; the distillation residue consists of a small amount of a viscid *resin* which boils at a high temperature and is probably a polymerisation product of the ether. Ethyl propenyl ether forms a volatile, mobile, transparent liquid, b. p. 69°, D_0^0 0·7951, or D_0^{20} 0·7754, is hygroscopic although only slightly soluble in water, is miscible with alcohol or ether, and rapidly decolorises potassium permanganate.

As β-ethoxyacrylic acid when boiled decomposes slowly, forming carbon dioxide and ethyl vinyl ether, the decomposition of β-alkoxy-acids of the acrylic series seems to be a general method for the preparation of mixed ethers of unsaturated alcohols. G. Y.

Structure of Phosphorous Acid and its Derivatives. ALEXANDER E. ARBASOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 161—228. Compare Abstr., 1905, i, 316).—A summary of previous work on the structure of phosphorous acid and its esters is given. It is not possible to separate the two esters, $P(OC_4H_9)_3$ and $P(OC_4H_9)_2 \cdot OH$, derived from *iso*butyl alcohol, owing to the proximity of their boiling points. In ascending the homologous series, the difference between the boiling points of the normal and acid esters steadily diminishes. The esters of phosphorous acid boil at a lower temperature than the corresponding arsenious esters. The preparation and purification of the compounds are described in detail. The formation of the esters $P(OR)_2 \cdot OH$ simultaneously with the normal esters in the action of alkali ethoxides on phosphorus trichloride is probably due to the presence of alkali hydroxide in the ethoxide employed, phosphorous acid being thus produced. The formation of the esters $PO(OR)_3$ has not been explained. Z. K.

Two Cases of Catalysis which are in agreement with Euler's Theory. ROBERT KREMANN (*Chem. Centr.*, 1906, ii, 1246; from *Verh. Ges. Deut. Naturf. Aerzte*, **77**, ii, 83—86).—Euler's explanation of catalytic action as due to an increase in the concentration of the reacting ions is confirmed by the following observations. The velocity of hydrolysis of esters by sodium ethoxide in absolute alcohols is very small, whereas the addition of 1% of water to propyl alcohol increases the velocity tenfold. When the acetates of polyhydric alcohols are hydrolysed by means of alcoholic sodium hydroxide, an 80—90% yield of ethyl acetate is formed almost at once; the sodium hydroxide here acts as a catalytic agent. The esters of monatomic alcohols of high molecular weight when heated with sodium hydroxide in alcoholic solution are decomposed with the formation of the ester of the alcohol which is acting as the solvent; this change, which takes place very slowly in the absence of alkali, is accelerated by its addition owing to the increase in the concentration of the reacting ions thereby produced, Ethyl acetate and glycerol in the same way give glyceryl acetate on the addition of alcoholic sodium hydroxide. P. H.

Resolution of α-Bromo*iso*hexoic and of α-Bromohydrocinnamic Acids. Emil Fischer and Hans Carl (*Ber.*, 1906, **39**, 3996—4003).—α-Bromo*iso*hexoic acid is resolved into its components by means of the brucine salts. l-*α-Bromo*iso*hexoic acid*, b. p. 94°/0·2—0·4 mm. (corr.), $[\alpha]_D^{20} - 49·43°$, with aqueous ammonia yields *d*-leucine having $[\alpha]_D^{20} - 14·20°$. *d-α-Bromo*iso*hexoic acid*, $[\alpha]_D^{20} + 48·99°$, with aqueous ammonia yields *l*-leucine having $[\alpha]_D^{20} + 13·92°$. A more convenient but less efficient method of preparing these active acids from leucine has been described (Abstr., 1906, i, 808).

α-Bromohydrocinnamic acid is resolved by means of its brucine or quinine salts, and by Ramberg's method (Abstr., 1906, i, 923). The solid acid necessary for the latter method is obtained by distilling benzylbromomalonic acid under 0·2—0·5 mm. pressure; the α-bromohydrocinnamic acid solidifies in needles, m. p. 48—49°, b. p. 138—141°/0·2 mm., D^{20} 1·48.

l-*α-Bromohydrocinnamic acid*, $[\alpha]_D^{20} - 8·3°$, is converted by aqueous ammonia into *d*-phenylalanine having $[\alpha]_D^{20} + 31·78°$. d-*α-Bromohydrocinnamic acid* has $[\alpha]_D^{20} + 7·9°$. C. S.

The "Alcoholysis" of Fatty Substances. Albin Haller (*Compt. rend.*, 1906, **143**, 657—661).—The author applies the term "*alcoholysis*" to the breaking down of a fat into glycerol and an alkyl ester of the fatty acid by heating it with the corresponding absolute alcohol containing a small quantity of mineral acid. This forms a convenient method for separating the fatty acids of (i) oils or fats which contain besides olein only glyceryl esters of saturated fatty acids such as butter, cocoa butter, suet, &c.; (ii) drying oils, such as linseed or poppy oil; (iii) oils containing glyceryl salts of hydroxy-acids, such as ricin. For this purpose the fat, previously dried, is heated in a reflux apparatus with its own weight of absolute methyl alcohol containing 1—2°/₀ of hydrogen chloride until the mixture becomes homogeneous, it is then poured into water or a brine solution, the methyl esters of the acids are removed by decantation or extracted with ether, washed with sodium carbonate solution, dried, and separated by fractional distillation in the case of acids of the series $C_nH_{2n}O_2$ up to $n = 12$, whilst the separation of methyl oleate, which is a liquid at the ordinary temperature, from methyl myristate, palmitate, or stearate, is effected by crystallisation at low temperature and subsequent draining of the crystals on porous plates at 0°.

It is possible that the process of *alcoholysis* may consist in a preliminary hydrolysis of the fat by the water produced by the action of the catalytic mineral acid on the alcohol, and a subsequent etherification of the fatty acid thus produced by the alcohol. M. A. W.

Observations Relating to Ethereal Equilibrium, and to the Mutual Displacement of Glycerol and the other Alcohols. Marcellin Berthelot (*Compt. rend.*, 1906, **143**, 717—718. Compare Haller, preceding abstract).—The author refers to his early work on the mutual displacement of glycerol and the other alcohols in the ethereal salts of the fatty acids (*Ann. Chim. Phys.*, 1854, [iii], **41**), and to the accelerating action of hydrochloric or other acids on the reaction; and objects to the use of the terms "hydrolysis" or "alcoholysis," on the ground that they are synonymous with the older expressions, "decompositions effected by water or alcohol." M. A. W.

Alcoholysis of Cocoa Butter. ALBIN HALLER and YOUSSOUFIAN (*Compt. rend.*, 1906, **143**, 803—806).—A specimen of cocoa butter having the following physical constants: solidifying point 21—20·5°; m. p. 23—25°; saponification number, 242·1; Reichert-Meissel number, 6·5; Hehner number, 90·5, and iodine number, 8·47, was treated with methyl alcohol containing 2 % hydrochloric or phenylsulphonic acid at 35°, and by the "*methanolysis*" thus effected the following methyl esters were formed: methyl hexoate, b. p. 52—53°/15 mm.; methyl octoate, m. p. –40—41°, b. p. 83°/15 mm.; methyl decoate, m. p. –18°, b. p. 114°/15 mm.; methyl laurate, m. p. 5°, b. p. 141°/15 mm.; methyl myristate, m. p. 18°, b. p. 167—168°/15 mm.; methyl palmitate, m. p. 28°, b. p. 196°/15 mm.; methyl stearate, m. p. 38°, b. p. 214—215°/15 mm., and methyl oleate, b. p. 212—213°/15 mm.; there was no trace of methyl butyrate, and similar results were obtained with two other specimens of cocoa butter from different sources. Cocoa butters therefore consist of the glyceryl esters of the C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}, and C_{18} saturated fatty acids and oleic acid, the esters of lauric and myristic acids preponderating (compare Lewkowitsch; Reijst, Abstr., 1906, ii, 403; Ulzer, *Chem. Revue*, 1899, 203). M. A. W.

The Theory of Saponification. JULIUS LEWKOWITSCH (*Ber.*, 1906, **39**, 4095—4097).—A reply to Marcusson (Abstr., 1906, i, 924). G. Y.

The Rôle of Metallic Hydrides in Reduction, and Data as to the Composition of Some Fats and Oils. SERGIUS FOKIN (*Zeit. Elektrochem.*, 1906, **12**, 749—762).—The electrolytic reduction of oleic acid to stearic acid was investigated. In the course of these experiments it was noticed that the yield of stearic acid is much improved by the presence of nickel. The most active nickel is that deposited as a fine black powder on the cathode or that obtained by reducing the oxide by hydrogen at 300—360°. It was found that iron or carbon brings about no reduction; experiments on the action of other metals were, therefore, made with an iron gauze or carbon cathode in a porous cell containing the solution of oleic acid in alcohol or acetone, the other metal being added in fine powder. It was found that platinum is more active than nickel and that palladium is more active still. Cobalt and copper also bring about the reduction. Silver, lead, mercury, manganese, chromium, zinc, bismuth, tungsten, vanadium, and aluminium are inactive. Iron occasionally gave a positive result.

Reduction of an alcoholic solution of oleic acid was also observed by treating the solution with palladium or platinum black and zinc and sulphuric acid or with reduced nickel or cobalt and magnesium and hydrochloric acid. Similar experiments with copper gave negative results.

An alcoholic solution of oleic acid is also reduced by boiling it with palladium hydride in a current of hydrogen. Nickel, reduced by hydrogen at 320°, gave no reduction under these conditions, but when the temperature was raised by using amyl alcohol, slow reduction took place. By using glycerol as solvent the temperature could be raised to 250°, and a rapid reduction was observed.

The author considers that in all cases the reduction depends on the formation of a hydride of the metal.

The methods of reduction described are applied to some natural oils and fats, such as linseed oil, Chinese wood oil, castor oil, and fish oil. From the nature of the saturated fatty acids obtained, conclusions may be drawn as to the unsaturated acids in the original oils.

Crotonic, angelic, fumaric, and cinnamic acids, allyl alcohol, and carbon tetrachloride were also reduced both electrolytically and by the zinc or magnesium-palladium couple. The last-named substance yields chloroform together with lower chlorination products of methane. T. E.

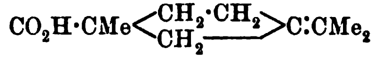
Constitution of Oleic Acid, &c. CARL D. HARRIES (*Ber.*, 1906, **39**, 3728—3732).—Polemical. A reply to Molinari and Soncini (Abstr., 1906, i, 792). A. McK.

Hydrolytic Products of Oleic Acid Ozonide. CARL D. HARRIES and HANS O. TÜRK (*Ber.*, 1906, **39**, 3732—3737. Compare Harries and Thieme, Abstr., 1906, i, 226; Molinari and Soncini, *ibid.*, i, 792).—The hydrolysis of the ozonides of oleic acid by water has been studied quantitatively; 15 grams of the viscid ozonide yield 2·0 grams of nonaldehyde, 4·2 grams of pelargonic acid, 4·4 grams of a mixture of azelaic acid and its semi-aldehyde, and 3·7 grams of a distillation residue which, on esterification by Fischer's method, yields the ethyl ester of azelaic acid and the ester-acetal of the semi-aldehyde of this acid, leaving only 1·5 grams of the ozonide unaccounted for. The product of the hydrolysis of 24 grams of the mobile ozonide of oleic acid contains 2·4 grams of nonaldehyde, 5·7 grams of pelargonic acid, 6·5 grams of distillation residue, 5 grams of azelaic acid, and 3·5 grams of the semi-aldehyde of azelaic acid. G. Y.

Constitution of the β-Fencholenic Acid Series. FRIEDRICH W. SEMMLER and KONRAD BARTELL (*Ber.*, 1906, **39**, 3960—3964).—Silver β-fencholenate and methyl iodide yield the *methyl* ester, $C_9H_{15}\cdot CO_2Me$, b. p. 97—99°/10 mm., D^{22} 0·9608, and n_D^{20} 1·46459. By reduction with sodium and alcohol, the *alcohol*, $C_{10}H_{18}O$, is obtained, b. p. 106—108°/10 mm., D^{22} 0·9272, and n_D^{20} 1·48033.

When β-fencholenolactone is shaken with dilute sodium hydroxide for twenty-four hours, *hydroxydihydrofencholenic acid*, $C_{10}H_{18}O_3$, is obtained, m. p. 110° (compare Mahla, Abstr., 1902, i, 106).

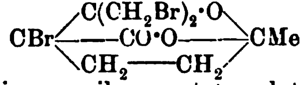
β-Fencholenic acid is oxidised by ozone to a ketonic *acid*, $C_7H_{10}O_3$, b. p. 166—170°/12 mm., D^{16} 1·1533, n_D 1·472, α 13·15°, which forms a *semicarbazone*, $C_8H_{13}O_3N_3$, m. p. 198—199°, and an *oxime*, m. p. 145°. By oxidation with neutral or faintly alkaline potassium permanganate, the ketonic acid is converted into a tricarboxylic acid, which by distillation in a vacuum loses carbon dioxide and forms α-methylglutaric acid.

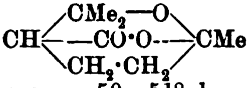
A table is given showing how the preceding compounds are derivable from fenchone by the use of Semmler's fenchone formula, that of β-fencholenic acid being  $CO_2H{\cdot}CMe{<}{{CH_2{\cdot}CH_2}\atop{CH_2\text{——}}}{>}C{:}CMe_2$. C. S.

Cineolic Acid. V. Cineolic Anhydride and Bromine. **Hans Rupe** and **Walther Lotz** (*Ber.*, 1906, **39**, 4076—4083. Compare Abstr., 1899, i, 340; 1900, i, 371; 1901, i, 119, 578; 1905, i, 409). —In absence of a solvent, the action of bromine on cineolic anhydride takes place with explosive violence, but in chloroform solution leads to the formation of carbon monoxide, two isomeric, crystalline *bromo*-compounds, $C_9H_{11}O_3Br_3$, which are separated by fractional crystallisation from methyl alcohol, and a yellow to brown oily product.

The *bromo*-compound, m. p. 156—157°, which is the less soluble in methyl alcohol, separates from alcohol in strongly doubly-refracting, white needles, as a granular, crystalline powder, or in small, glistening, rhombic plates [$a : b : c = 0{\cdot}7341 : 1 : 0{\cdot}7686$].

The *bromo*-compound, m. p. 129°, crystallises from methyl alcohol in large, rhombic plates [$a : b : c = 0{\cdot}68256 : 1 : 0{\cdot}65989$].

These bromo-compounds, one of which, if not both, must have the constitution , remain unchanged when boiled with potassium or silver acetate solution or with alcoholic hydrogen chloride, and are insoluble in cold alkali hydroxide or carbonate solutions, but when boiled with these or with aqueous baryta are converted into an *acid*, $C_9H_{12}O_4$ or $C_9H_{14}O_4$, m. p. 172—174°, which is stable towards potassium permanganate.

Reduction of the bromo-compounds with zinc dust and alcohol leads to the formation of a δ-lactone, , which crystallises in transparent, white plates, m. p. 50—51°, b. p. 117—118·5°/14 mm. or 126—128°/20 mm., has a bitter taste, reddens litmus in aqueous solution, is not extracted from its ethereal solution by aqueous potassium carbonate, and only very slowly so by aqueous sodium carbonate. It is stable towards potassium permanganate, dissolves in concentrated sulphuric acid, forming a colourless solution, and decomposes at 170° under the ordinary pressure, forming carbon dioxide and methylheptenone.

The oily product from the action of bromine on cineolic anhydride readily resinifies, decomposes when distilled in a vacuum, and when reduced yields to some extent the same products as do the crystalline bromides, but with stannous chloride and alcoholic hydrogen chloride forms an *ester* from which cineolic acid is obtained on hydrolysis; when boiled with aqueous sodium hydroxide, the oily bromo-compound yields a small amount of an *acid*, m. p. about 172°, which is stable towards potassium permanganate, does not contain bromine, and may be identical with the acid obtained from the crystalline bromo-compounds. G. Y.

Cineolic Acid. VI. Action of Sulphuric Acid on Cineolic Acid. Hans Rupe and Walther Lotz (*Ber.*, 1906, **39**, 4083—4086. Compare preceding abstract; Bistrzycki and Reintke, Abstr., 1905, i, 285; Bistrzycki and Siemiradzki, Abstr., 1906, i, 135).—The lactone, $C_9H_{14}O_3$, m. p. 50—51° (see preceding abstract), is formed together with carbon monoxide when cineolic acid, or in a 90% yield when cineolic anhydride, is treated with concentrated sulphuric acid at the laboratory temperature.

2:4-Dimethylbenzoic acid is formed by heating the lactone, or cineolic acid or its anhydride with concentrated sulphuric acid on the water-bath.

2:4-*Dimethylbenzoyl*-p-*toluidide*, prepared by heating the acid with *p*-toluidine at 200—220°, crystallises in glistening, silky needles, m. p. 152°.

The action of zinc chloride on the lactone at 110° leads to the formation of dihydro-*m*-xylene, b. p. 132—134·5°, n_D^{20} 1·46867 (Wallach and Gildemeister, Abstr., 1888, 1205), and of a small amount of 2:4-dimethylbenzoic acid. G. Y.

Reversible Conversion of Paraformaldehyde into Formaldehyde, and Sterilisation with Formaldehyde at High Temperatures. Léon Perdrix (*Ann. Inst. Pasteur*, 1906, **20**, 881—900).—The curve representing the vapour tension of the transformation of paraformaldehyde into formaldehyde rises very rapidly with the temperature. This fact must be taken into account when using formaldehyde as a sterilising agent, an operation which should be carried out preferably at a moderately high temperature. The use of anhydrous formaldehyde is preferable to that of formol as a sterilising agent on account of the greater vapour pressure of the latter. Experiments made with anhydrous formaldehyde at 100° on various bacteria which are not easily destroyed by ordinary methods of sterilisation showed this to be in every case a very effective agent. E. F. A.

Chlorination of Paracetaldehyde; Butylchloral. Paul Freundler (*Compt. rend.*, 1906, **143**, 682—684).—Pinner has shown that the chlorination of paracetaldehyde results in the formation of butylchloral (Abstr., 1876, 552. Compare Lieben, Abstr., 1883, 963), and the author finds that tetrabromobutaldehyde is the product of the bromination of paracetaldehyde (Abstr., 1905, i, 569). In each case the first product of the reaction is the corresponding monohalogen derivative of acetaldehyde, which in the case of the chloro-compound condenses at the ordinary temperature with the unchanged acetaldehyde to form α-chlorocrotonaldehyde; this on further chlorination yields butylchloral; whilst under similar conditions of temperature 2 mols. of bromoacetaldehyde condense to form α-γ-dibromocrotonaldehyde, which on further bromination yields tetrabromobutaldehyde.

Butylchloral hydrate, like chloral or bromal hydrate, behaves as a dibasic acid; the *acetal*, $CH_3·CHCl·CCl_2·CH(OEt)_2$, boils at 122—124°/20—21 mm.; the *ethyl ether* of the acetamide derivative [*ethyl a-acetylamino-ββγ-trichlorobutyl ether*],

$$CH_3·CHCl·CCl_2·CH(NHAc)·OEt,$$

m. p. 86°, b. p. 163—164°/15—16 mm., crystallises from benzene and light petroleum in prisms. Contrary to Schiff's experience (Abstr., 1892, 1067), the author obtained only one acetamide and one benzamide derivative of butylchloral, m. p. 206—208° and 176—178° respectively, and not 170° and 148° as stated by Schiff. M. A. W.

Methylethylacetaldehyde [α-Methylbutaldehyde] and some of its Condensation Products. VIKTOR NEUSTÄDTER (*Monatsh.*, 1906, **27**, 879—934. Compare Lieben, Abstr., 1901, i, 449).—Of the aldehydes containing only one α-hydrogen atom, *iso*butaldehyde alone has been fully investigated. This paper gives the results of the study of a second member of the same group.

α-Methylbutaldehyde (methylethylacetaldehyde) was present probably in the valeraldehyde prepared from commercial amyl alcohol and utilised by Kohn (Abstr., 1896, i, 10; 1897, i, 396), Lederer (Abstr., 1901, i, 669), Rosinger (*ibid.*), and Morgenstern (Abstr., 1903, i, 787).

α-Methylbutaldehyde is prepared from methyl ethyl ketone by reduction to *sec.*-butyl alcohol, successive conversion of this into *sec.*-butyl bromide, and by means of Grignard's reaction with formic acid, *sec.*-butylcarbinol (Rainer, Abstr., 1905, i, 16), and finally by oxidation of the carbinol by means of potassium dichromate and dilute sulphuric acid.

The preparation of the aldehyde by Claisen's method (Abstr., 1905, i, 286) from methyl ethyl ketone by way of ethyl β-methyl-β-ethylglycidate also is described. On distillation in a current of steam the glycidic acid is only partially decomposed to the aldehyde, the main portion forming the *dihydroxy-acid*, $OH·CMeEt·CH(OH)·CO_2H$; this is obtained as a greenish-yellow, viscid mass, which on distillation under atmospheric pressure decomposes at about 185°, forming carbon dioxide, water, and α-methylbutaldehyde, the total yield of which amounts to 85 % of the sodium methylethylglycidate.

When treated with hydrogen chloride in a freezing mixture, α-methylbutaldehyde forms the *polymeride*, $(C_5H_{10}O)_3$, which is obtained as a mobile oil having a characteristic odour, b. p. 133°/20 mm., and yields the monoaldehyde when boiled with a small amount of concentrated sulphuric acid. The absence of *iso*valeraldehyde is shown by a determination of the solubility of the silver salt obtained on boiling the aldehyde with silver oxide and water (compare Sedlitzky, Abstr., 1888, 250).

The action of alcoholic potassium hydroxide on α-methylbutaldehyde cooled by ice, and finally at the ordinary temperature, leads to the formation of α-methylbutyric acid and the *glycol*,

$$CHMeEt·CH(OH)·CMeEt·CH_2·OH;$$

this is obtained as a viscid, colourless liquid, b. p. 133°/10 mm., and has a sp. gr. less than that of water. It solidifies when cooled in a mixture of ether and carbon dioxide, has a cooling taste, and is readily soluble in absolute alcohol, ether, light petroleum, or benzene, but only sparingly so in water or aqueous alcohol.

A colourless, viscid liquid, b. p. 90°/20 mm., obtained by the action of solid potassium carbonate on α-methylbutaldehyde in a sealed tube at 155°, or of a very small amount of alcoholic potassium hydroxide on the aldehyde in the cold, is probably the *aldol*,

CHMeEt·CH(OH)·CMEt·COH.

The action of metallic sodium on α-methylbutaldehyde at 18—24° leads to the formation of the glycol $C_{10}H_{22}O_2$ and of two esters, b. p. 70—72°/11 mm., and 162—165°/11 mm. respectively.

*iso**Amyl α-methylbutyrate*, $CHMeEt\cdot CO_2\cdot CH_2\cdot CHMeEt$, is a mobile, yellow liquid having a pleasant ethereal odour, b. p. 70—72°/11 mm., or 183—184°/741 mm., and is hydrolysed by boiling alcoholic potassium hydroxide.

The fraction, b. p. 162—165°/11 mm., contains the *ester*,

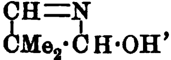
$$CHMeEt\cdot CO_2\cdot CH_2\cdot CMeEt\cdot CH(OH)\cdot CHMeEt,$$

which is formed also by the action of sodium ethoxide in absolute alcoholic solution, and probably in small amounts by that of potassium carbonate or potassium hydroxide on the aldehyde under various conditions. It is a colourless, mobile liquid having a slight ester odour, b. p. 272—274°/741 mm., and on hydrolysis with aqueous-alcoholic potassium hydroxide, yields the glycol $C_{10}H_{22}O_2$ and α-methylbutyric acid.

α-Methylbutaldoxime, $C_5H_{11}ON$, is obtained as a transparent, mobile oil, b. p. 149—151°/749 mm.; when heated with acetic anhydride in a sealed tube at 140°, it yields *α-methylbutyronitrile* as a colourless liquid, b. p. 125°/760 mm.

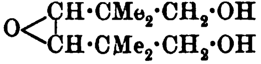
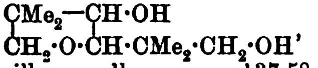
The *aldazine*, $N_2(CH\cdot CHMeEt)_2$, formed by the action of hydrazine sulphate and sodium carbonate on the aldehyde, is a mobile, ethereal, yellow liquid, b. p. 200—202° under the ordinary pressure; when treated with concentrated alcoholic hydrogen chloride in ethereal solution, it yields the aldehyde and hydrazine hydrochloride (compare Franke, Abstr., 1900, i, 212). G. Y.

Reduction of Formyl*iso*butaldol and its Oxime. RUDOLF BÖHM (*Monatsh.*, 1906, 27, 947—962. Compare Wessely, Abstr., 1900, i, 428).—When distilled under atmospheric pressure, the oxime of formyl*iso*butaldol decomposes, yielding water, an oil which on redistillation gives two fractions, b. p. 65°/34 mm. and 120°/34 mm. respectively, together with a small amount of a *substance* which crystallises in rhombic prisms, m. p. 117°, is more soluble in water than in ether, and evolves ammonia when heated with aqueous sodium hydroxide.



The fraction, b. p. 65°/34 mm., consists of the *anhydride* of the oxime, $\begin{array}{l}CH{=\!=}N\\ \mid \qquad\;\; \mid\\ CMe_2\cdot CH\cdot OH\end{array}$, which is obtained as a colourless oil, b. p. 57°/9 mm. or 137°/760 mm.; it has a pleasant ethereal odour, yields formyl*iso*butaldol when heated with 10°/₀ hydrochloric acid, and reacts with sodium with evolution of hydrogen or with acetic acid with development of heat.

The fraction, b. p. 120°/34 mm., contains *aa-dimethylhydracrylonitrile*, which forms a colourless oil, becoming brown on exposure to air, b. p. 97°/11 mm., or 103°/15 mm.; when boiled with 15°/₀ hydrochloric acid, it yields hydroxypivalic acid, the *calcium* salt, $C_{10}H_{18}O_6Ca$, of which is described. The *acetate* of *aa*-dimethylhydracrylonitrile, $C_7H_{11}O_2N$, formed by the action of acetic anhydride and sodium acetate on the oxime of formyl*iso*butaldol, is obtained as a colourless oil having a pleasant ethereal odour, b. p. 91·5°/11 mm. or 97°/15 mm.; on hydrolysis it yields hydroxypivalic acid. Oxidation of the acetate with potassium permanganate in aqueous solution leads to the formation of *a-cyano*iso*butyric acid*, $CN\cdot CMe_2\cdot CO_2H$, which is formed also together with *iso*butyric acid by the oxidation of *a*-dimethylhydracrylonitrile; it crystallises in large, white leaflets, m. p. 56—57°.

Formyl*iso*butaldol is reduced by sodium amalgam, forming the corresponding pentaglycol, or by zinc and hydrochloric acid, yielding two *products*, which must be formed by loss of water from hydrobenzoin-like derivatives of the aldol, and are separated by fractional recrystallisation from alcohol: (*a*)  $O<\begin{matrix}CH\cdot CMe_2\cdot CH_2\cdot OH\\ |\\ CH\cdot CMe_2\cdot CH_2\cdot OH\end{matrix}$ or  $\begin{matrix}CMe_2-CH\cdot OH\\ |\qquad\ \ |\\ CH_2\cdot O\cdot CH\cdot CMe_2\cdot CH_2\cdot OH\end{matrix}$, crystallises from alcohol in glistening, silky needles, m. p. 137·5°, and forms a *diacetyl* derivative crystallising in long, flat, white needles, m. p. 87°; (*b*) $C_{10}H_{20}O_3$, crystallises in large prisms or long, slender spears, m. p. 63·5°. If the reduction with zinc and hydrochloric acid is carried out at higher temperatures, a third *product* crystallising in glistening plates, m. p. 184°, is formed.

Electrolytic reduction of the aldol in 30—31°/₀ sulphuric acid solution with a lead cathode and a carbon anode and a current density of 2 amperes per square decimetre leads to the formation of oily products only, but with a current density of 5 amperes per square decimetre to the formation also of the two crystalline products, m. p. 63·5° and 137·5° respectively. G. Y.

The Pinacolin from the Pinacone of Methyl Ethyl Ketone.

BERTA BRAUN and HANS KITTEL (*Monatsh.*, 1906, **27**, 803—821).—Glücksmann (Abstr., 1892, 38) and Schindler (Abstr., 1893, i, 71) found that the action of 90°/₀ sulphuric acid on *β*-trimethylethylidenelactic acid leads to the formation of methyl *iso*propyl ketone and not to that of the expected aldehyde. The object of the present work is to compare the behaviour of an homologous lactic acid.

Reduction of methyl ethyl ketone by means of sodium in ethereal solution under an aqueous solution of potassium carbonate leads to the formation of *sec.*-butyl alcohol (65°/₀), pinacone (10—12°/₀), and an analogue of phorone (12°/₀), b. p. 256° (compare Schramm, Abstr., 1883, 1079), 10°/₀ of the ketone remaining unchanged.

The substance, $CMeEt:C_2H_3\cdot CMe:C_2H_3\cdot COMe$, b. p. 256°, is a slightly yellow oil, forms an *additive* compound with 2 mols. of bromine, and yields an *oxime*, $C_{12}H_{20}:N\cdot OH$, b. p. 260°.

On oxidation with potassium permanganate in aqueous sodium hydroxide solution, the pinacolin, b. p. 148—154°, obtained by boiling pinacone with 10°/₀ sulphuric acid (compare Zelinsky and Krapiwin, Abstr., 1893, i, 390; Herschmann, *ibid.*, 547), yields an *acid*, $C_8H_{14}O_3$, together with small amounts of acetic and *aa*-dimethylbutyric acids.

β-Keto-γγ-dimethylhexoic acid, $CMe_2Et{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$, forms a *silver* salt, $C_8H_{13}O_3Ag$, crystallising in long needles, and is reduced with sodium amalgam and water, yielding the *β-hydroxy*-acid,

$$CMe_2Et{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H,$$

which crystallises in small plates, m. p. 82°, and is not volatile in a current of steam; the crystalline *silver*, $C_8H_{15}O_3Ag$, and *potassium* salts were analysed. When heated with concentrated phosphoric acid and lead dioxide, the β-hydroxy-acid evolves a gas, and on distillation in a current of steam yields an acid distillate.

The action of boiling 90°/₀ sulphuric acid on β-hydroxy-γγ-dimethylhexoic acid leads to the formation of methyl *aa*-dimethylpropyl ketone, b. p. 131—132°. No trace of an aldehyde could be found in the sulphuric acid solution. G. Y.

Fermentation of Sugar without Enzymes. EDUARD BUCHNER, JAKOB MEISENHEIMER, and H. SCHADE (*Ber.*, 1906, **39**, 4217—4231).—Contrary to Schade's statement that sugars in alkaline solution are decomposed by air or hydrogen peroxide, yielding equal molecular quantities of formic acid and acetaldehyde (or acetic acid) (Abstr., 1906, i, 931), the authors find that the acid products of decomposition, in the case of lævulose, are formic, glycollic, and *i*-erythritic acids; acetic, lactic, and oxalic acids are not formed. Hydrogen is evolved, probably in accordance with the equation $2CH_2O + H_2O_2 = 2H{\cdot}CO_2H + H_2$, the formaldehyde being an initial product of the decomposition of the sugar. C. S.

Connexion between the Chemical Nature of the Amines and their Power to form Complex Compounds. LEO A. TCHUGAEFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 9—12. Compare Abstr., 1905, i, 865).—In order to ascertain how far the observations previously made regarding the behaviour of the amines towards copper succinimide could be applied to other analogous cases, the action of various amines towards copper chloride, silver nitrate, potassium platinosochloride, and platinic chloride has been investigated. The results completely confirm those previously found. The primary amines easily form complexes, the secondary do so much less readily, whilst the tertiary do not yield complex compounds, but the inorganic salt is often reduced. Contrary to the generally accepted view as to these reactions, it is considered that the reactivity of the amines depends, to a very large extent, on the number of free hydrogen atoms attached directly to the nitrogen atom. The reason Jörgensen adopted the opposite view was that he employed pyridine, which, being a heterocyclic amine, forms an exception to the general rule; the latter also only holds for those cases in which the amine as such forms the compound, or, according to Abegg, the neutral part of a complex ion, but the tertiary amines, just like the primary or secondary, easily enter into binary combinations when they form complex ammonia radicles.

Z. K.

Salts of Quaternary Ammonium Bases with Organic Acids. Tetramethylammonium Formate. L. Vanzetti (*Chem. Centr.*, 1906, ii, 1347; from *Boll. Chim. Farm.*, **45**, 593—598).—*Tetramethylammonium formate* (*Forgenin*), $H\cdot CO_2\cdot NMe_4$, obtained by the action of tetramethylammonium iodide on silver formate, is a white crystalline, odourless, hygroscopic substance, which gives the reactions of formates, and evolves carbon monoxide on warming with sulphuric acid. It is stable in dry air or in solution, but decomposes at above 200°. Unlike other quaternary bases its physiological action does not resemble that of curare. P. H.

Novaine. Friedrich Kutscher (*Zeit. physiol. Chem.*, 1906, **49**, 47—49).—When a concentrated solution of novaine hydrochloride is distilled with crystallised barium hydroxide, trimethylamine is formed, and if the operation is repeated some twelve times with the addition of fresh amounts of water, practically the whole of the nitrogen is evolved in this form. This reaction indicates that novaine is closely related to the choline bases. It is probably a higher homologue of muscarine, and the formula $OH\cdot NMe_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(OH)_2$ is suggested. The oblitine molecule probably contains two novaine residues.

J. J. S.

Stereochemistry of 2:5-Diketopiperazines. Emil Fischer and Karl Raske (*Ber.*, 1906, **39**, 3981—3995).—Mainly an account of work already published (compare Abstr., 1906, i, 457).

d-*Bromopropionyl*-l-*alanine*, $C_6H_{10}O_3NBr$, obtained from *l*-alanine in a similar manner to its optical antipode, separates from hot water in octahedra, m. p. 170°, decomposing, $[\alpha]_D^{20} + 67\cdot91°$, and by treatment with aqueous ammonia yields d-*alanyl*-l-*alanine*, which closely resembles its optical isomeride, differing in m. p. 275—276° (corr.) and $[\alpha]_D^{20} + 68\cdot94°$, and yields *trans*-alanine anhydride. By hydrolysis with hydrochloric acid at 100°, the dipeptide yields racemic alanine hydrochloride.

d-α-*Bromopropionic acid* is obtained readily from *l*-alanine in a similar manner to the *l*-acid (compare Abstr., 1905, i, 692), and has $\alpha_D^{20} + 44\cdot2°$. C. S.

Action of Nitrous Acid on Lysine. Leo Szydlowski (*Monatsh.*, 1906, **27**, 821—830. Compare Fischer and Tiemann, Abstr., 1894, i, 167; Fischer and Weigert, Abstr., 1902, i, 352; Neuberg and Wolff, Abstr., 1903, i, 74).—The action of barium or silver nitrite on lysine sulphate or hydrochloride in aqueous solution cooled by ice leads to the formation of αε-dihydroxyhexoic acid, an aminohydroxyhexoic acid, and a small amount of an alkaline, yellow, amorphous substance, $C_6H_{13}O_3N$, m. p. 176—178°.

αε-*Dihydroxyhexoic acid* is isolated in the form of its *calcium* salt, $Ca(C_6H_{11}O_4)_2$.

The aminohydroxyhexoic acid crystallises in needles, m. p. 200—201°, and may be identical with Fischer and Tiemann's and Neuberg and Wolff's acids. G. Y.

Action of Magnesium Bromide and Iodide on some Derivatives of Carbamide. VII. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 4).—Urethane reacts readily with both the iodide and bromide of magnesium, forming the *compounds*

$$MgBr_2,6NH_2\cdot CO_2Et$$

and $MgI_2,6NH_2\cdot CO_2Et$; the eutectic point of the system lies at 35°. The solubility curve of the *compound* $MgBr_2,6NH_2\cdot CO_2Et$, in presence of traces of the *compound* $MgBr_2,,4NH_2\cdot CO_2Et$, is broken at 91° when the system $MgBr_2,6\cdot55NH_2\cdot CO_2Et$, is formed, but when the lower compound is completely absent, the melting point of the *compound* $MgBr_2,6NH_2\cdot CO_2Et$, 91·5°, can be reached. The solubility curve of the *compound* $MgBr_2,4NH_2\cdot CO_2Et$ in urethane ends at its melting point, 123°, which is again lowered by any further addition of magnesium bromide. The system magnesium iodide-urethane gives similar results, but the eutectic point, 32°, is lower, as is also the melting point, 87°, of the *compound* $MgI_2,6NH_2\cdot CO_2Et$. Carbamide forms *compounds* with magnesium bromide equally well. The eutectic point is 108°. At 130·5° there is a break in the solubility curve, at the composition $MgBr_2,9\cdot21CO(NH_2)_2$. The next curve continues to 170°, when decomposition occurs. Probably the first curve corresponds with the *compound* $MgBr_2,6CO\cdot(NH_2)_2$, and the second with the *compound* $MgBr_2,4CO(NH_2)_2$. Z. K.

Compounds of Magnesium Bromide with Derivatives of the Acids. VI. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 3).—As the amount of magnesium bromide is increased in the system magnesium bromide–acetamide, the m. p. of acetamide (82°) is lowered until the eutectic point 50·5° is reached, the composition of the system then being $MgBr_2,13\cdot17COMe\cdot NH_2$. The solubility curve of the *compound* $MgBr_2,6COMe\cdot NH_2$ in acetamide ends at 169°, its m. p. On further addition of magnesium bromide, the m. p. is at first lowered to 136°, corresponding with the *compound* $MgBr_2,3\cdot75COMe\cdot NH_2$, it then again rises to 160°, the m. p. of the *compound* $MgBr_2,2COMe\cdot NH_2$, but it is not quite certain whether a compound containing 2 mols. of acetamide is really formed. Acetanilide with magnesium bromide yields the *compound* $MgBr_2,6COMe\cdot NHPh$. The eutectic point lies 4·5° lower than its m. p., 112°. The solubility curve of this compound in acetanilide ends at 209°, its m. p., and any further addition of magnesium bromide gives results similar to those with acetamide. Z. K.

Action of Hydrogen Cyanide on Aldehyde-Ammonia. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1906, **39**, 3942—3959. Compare Delépine, Abstr., 1904, i, 148).—When aldehyde-ammonia is acted on by a 3 °/₀ solution of hydrocyanic acid either in light or in the dark, the following substances are obtained: (1) two isomeric compounds, $C_6H_{12}O_3N_2$, of which the one more sparingly soluble in water than the other has m. p. 232°, whilst the isomeride has m. p. 210°; (2) a compound, $C_6H_{10}O_2N_2$, m. p. 186°, soluble in ether; (3) alanine; (4) an amorphous, indefinite compound.

The compound $C_6H_{12}O_3N_2$, m. p. 232°, is the monoamide of the α-iminodipropionic acid (m. p. 254—255°, termed by the authors A-α-iminodipropionic acid), whilst the isomeride $C_6H_{12}O_3N_2$, m. p. 210°, is the monoamide of the α-iminodipropionic acid (m. p. 234—235°; B-α-iminodipropionic acid). It is pointed out that the two isomeric α-iminodipropionic acids referred to bear the same relationship to one another as that which exists between racemic and mesotartaric acids.

The compound $C_6H_{10}O_2N_2$ is the imide of B-α-iminodipropionic acid.

A-α-Iminodipropionic monoamide (m. p. 232°) crystallises from water in hexagonal plates. Its aqueous solution gives an acid reaction and exhibits the biuret reaction. B-α-Iminodipropionic monoamide (m. p. 210°) separates in colourless prisms.

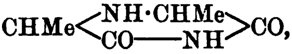
When the A-amide is boiled with baryta, it forms the *barium* salt, $(C_6H_{10}O_4N)_2Ba$, which crystallises in needles and yields the corresponding A-α-iminodipropionic acid. The latter forms a *hydrogen potassium* salt, $C_6H_{10}O_4NK$, which separates from aqueous alcohol in colourless prisms; the *silver double* salt, $C_6H_{10}O_4NAg,AgNO_3$, and the *silver* salt, $C_6H_9O_4NAg_2$, are described. The *diethyl* ester, $C_6H_9O_4NEt_2$, is a viscid oil, b. p. 123—124°/15 mm., which forms the *nitroso*-derivative, $C_6H_8O_4Et_2N{\cdot}NO$, a yellow oil, b. p. 177°/18 mm., giving a strong Liebermann reaction.

B-α-Iminodipropionic monoamide separates from water in prisms containing $1\frac{1}{2}H_2O$, and is more sparingly soluble in water than its isomeride. When boiled with baryta, it forms the *barium* salt,

$$C_6H_9O_4NBa;$$

the *hydrogen barium* salt, $(C_6H_{10}O_4N)Ba$, is also described. B-α-Iminodipropionic acid crystallises in prisms, m. p. 234—235°. The *compound* $(C_6H_{10}O_4NAg)_2,AgNO_3$ crystallises in leaflets; the *silver* salt is described; the *diethyl* ester, $C_6N_9O_4NEt_2$, is an oil, b. p. 121—122°/15 mm., m. p. −5°; which forms a *nitroso*-derivative, $C_6H_8O_4EtN{\cdot}NO$, an oil, b. p. 163—164°/17 mm., and giving a strong Liebermann reaction.

B-α-Iminodipropionic acid forms the imide



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{NH{\cdot}CHMe}\\ \mathrm{CO{-\!-}NH}\end{matrix}{>}\mathrm{CO},$$

which was isolated as one of the products of the action of hydrogen cyanide on aldehyde-ammonia; it separates from benzene in needles or prisms, m. p. 186°.

When the action of hydrogen cyanide on aldehyde-ammonia is conducted in the dark instead of in the light, the same products are formed, but in different proportions.

Experiments carried out by heating molecular amounts of aldehyde-ammonia and hydrocyanic acid (12%) at the temperature of a boiling water-bath, showed that Erlenmeyer and Passavant's α-iminopropionitrile (Abstr., 1880, 313) yields on hydrolysis alanine and A-α-iminodipropionic acid. A. McK.

Method of Preparing the Oxynitriles, $OR{\cdot}CH_2{\cdot}CN$. D. Gauthier (*Compt. rend.*, 1906, **143**, 831—832).—Chloromethyl alkyl ethers of the type $RO\cdot CH_2Cl$, prepared by the action of hydrogen chloride on a mixture of the corresponding alcohol ROH and formaldehyde (Henry), are readily converted into the corresponding cyanoalkyloxymethanes, $RO\cdot CH_2\cdot CN$, by the action of mercuric, or, preferably, cuprous cyanide; the reaction takes place in the cold, the yield is 60—70% of the theoretical, and the following compounds were thus prepared. *Methoxyacetonitrile*, $OMe\cdot CH_2\cdot CN$, b. p. 118—119°; *propoxyacetonitrile*, $C_3H_7O\cdot CH_2\cdot CN$, b. p. 147—148°; iso*butyloxyacetonitrile*, $C_4H_9O\cdot CH_2\cdot CN$, b. p. 158—160°; and *amyloxyacetonitrile*, $C_5H_{11}O\cdot CH_2\cdot CN$, b. p. 183—184°. M. A. W.

Nitriles of Alkylglycollic Acids [Cyanoalkyloxymethanes]. Marcel Sommelet (*Compt. rend.*, 1906, **143**, 827—828).—Cyanoalkyloxymethanes [alkyloxyacetonitriles] (compare Abstr., 1904, i, 222), originally prepared by dehydrating the corresponding alkyloxyacetamides by means of phosphoric oxide (Henry, Abstr., 1873, 879), are more conveniently obtained by the action of silver or mercuric cyanide on the corresponding chloromethyl alkyl ether, and the following compounds were thus prepared. *Methoxyacetonitrile*, $OMe\cdot CH_2\cdot CN$, prepared by the action of mercuric cyanide in the cold on chloromethyl methyl ether, is a colourless liquid, b. p. 120°, with an odour recalling that of ethyl formate. Ethoxyacetonitrile, $OEt\cdot CH_2\cdot CN$, b. p. 135·4°/760 mm., is prepared by the action of silver cyanide on chloromethyl ethyl ether; the yield is 70%. The following derivatives were also prepared: Ethoxyacetic acid, b. p. 156—157°; the *amide*, m. p. 82°, and the *thioamide*, m. p. 81°. *Propoxyacetonitrile*, $OPr^{\alpha}\cdot CH_2\cdot CN$, is a colourless liquid with a sweet odour, b. p. 151—152°/758 mm., the *thioamide*, m. p. 63°. iso*Butoxyacetonitrile*, $C_4H_9O\cdot CH_2\cdot CN$, is a colourless liquid, b. p. 80—82°/44 mm.; the *thioamide*, m. p. 60—61°. iso*Amyloxyacetonitrile*, $C_5H_{11}O\cdot CH_2\cdot CN$, is a colourless, slightly oily liquid with a strong odour, b. p. 99°/44 mm. M. A. W.

ψ-Diazoacetamide. Theodor Curtius, August Darapsky, and Ernst Müller (*Ber.*, 1906, **39**, 3776—3783. Compare Abstr., 1906, i, 939; Curtius and Lang, Abstr., 1889, 369; Curtius and Thompson, Abstr., 1906, i, 940; Pinner, Abstr., 1898, i, 94; Hantzsch and Silberrad, Abstr., 1900, i, 261; Hantzsch and Lehmann, Abstr., 1901, i, 678; Silberrad, Trans., 1900, **77**, 1185).—The constitutions of bisdiazoacetamide and ψ-diazoacetamide are discussed in the light of Bulow's paper (Abstr., 1906, i, 905). Bisdiazoacetamide is probably 1 : 2-dihydrotetrazine-3 : 6-dicarboxylamide, and ψ-diazoacetamide 3 : 6-dihydrotetrazine-3 : 6-dicarboxylamide, but a definite decision on these points or on the question of the existence of 1 : 4-dihydrotetrazine apart from 1-amino-1 : 3 : 4-triazole cannot yet be reached.

G. Y.

Syntheses with Azoimides. V. Diazoaminomethane (Dimethyltriazen). Otto Dimroth (*Ber.*, 1906, **39**, 3905—3912. Compare Abstr., 1905, i, 311).—The author describes the preparation of diazoaminomethane, a compound of special interest as being the simplest representative of the diazoamino-series. The isolation of the compound was attended with difficulties owing to its instability and to the fact that it is miscible with water in all proportions.

Diazoaminomethane is obtained by the action of magnesium methyl iodide on methylazoimide (compare Dimroth and Wislicenus, Abstr., 1905, i, 422) and decomposition of the resulting compound with water. Its formation is represented by the equations: (1) $MeMgI + Me{\cdot}N_3 = NMe{:}N{\cdot}NMe{\cdot}MgI$ and (2) $NMe{:}N{\cdot}NMe{\cdot}MgI + H_2O =$

$$NMe{:}N{\cdot}NHMe + MgI(OH).$$

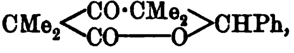
During its formation, diazoaminomethane is decomposed with evolution of nitrogen to an extent which may be lessened if the Grignard reagent be filtered from the impurities present in the commercial magnesium used, the latter impurities having a catalytic effect on the decomposition. The aqueous solution of diazoaminomethane was extracted with a large amount of ether, the copper compound formed and the latter dried and heated with an equivalent quantity of diazoaminobenzene in a glycerol bath, which was gradually raised to 100° whilst the pressure was maintained at about 200 mm. The action is represented by the equation $N_3Me_2Cu + N_3HPh_2 = N_3Me_2H + N_3CuPh_2$.

Diazoaminomethane (*dimethyltriazen*), N_3Me_2H, obtained by this method, is a colourless liquid which solidifies when immersed in a mixture of carbon dioxide and ether; m. p. −12°, b. p. 92°. When heated quickly, it explodes. It has unpleasant physiological effects. As distinct from aromatic and fatty-aromatic diazoamino-compounds, it is a base; it does not, however, form salts, since acids, even the weakest, decompose it with evolution of nitrogen. It reacts with hydrochloric acid according to the equation $N_3Me_2H + 2HCl = MeCl + N_2 + NH_2Me,HCl$, whilst with sulphuric acid it forms methyl hydrogen sulphate in an analogous manner. It decomposes in contact with finely-divided platinum. *Copper dimethyltriazen*, N_3Me_2Cu, separates from ether in glistening, yellow prisms, m. p. 185—186°; it is decomposed by dilute sulphuric acid. *Silver dimethyltriazen*, N_3Me_2Ag, forms colourless, silky needles.

Dimethyltriazen combines in ethereal solution with phenylcarbimide to form the *carbamide* $N_3Me_2{\cdot}CO{\cdot}NHPh$, which separates from light petroleum in needles or plates, m. p. 62°. A. McK.

The Action of Magnesium on Ethyl Bromo*iso*butyrate. Julius Salkind (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 97—103).—Magnesium alone acts very slowly on an ethereal solution of ethyl α-bromo*iso*butyrate, but the addition of a little iodine greatly facilitates the reaction whilst the presence of acetyl chloride retards it. The most probable final product of the reaction is *ethyl tetramethylacetoacetate*, containing a little bromine, b. p. 199—201°; its *semicarbazide* derivative, m. p. 136—137°. The reaction probably proceeds in the following stages: $2CMe_2Br{\cdot}CO_2Et \longrightarrow 2MgBr{\cdot}CMe_2{\cdot}CO_2Et \longrightarrow MgBr{\cdot}CMe_2{\cdot}C(OEt)(OMgBr){\cdot}CMe_2{\cdot}CO_2Et \rightarrow CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et.$ Z. K.

The Action of Magnesium on the Esters of Bromo-acids and on a Mixture of these Esters and Aldehydes. J. Zeltner and Sergius Reformatsky (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 103—109. Compare preceding abstract).—*Ethyl tetramethylacetoacetate* has been obtained by a slightly different method from that used by Salkind. The following is proposed as a possible alternative for the second and third stages of the reaction:

$2MgBr{\cdot}CMe_2{\cdot}CO_2Et = MgBr{\cdot}OEt + MgBr{\cdot}CMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$, which, with water, yields ethyl tetramethylacetoacetate (compare *ibid.*, 1905, **37**, 881). Semicarbazide gives with it a *crystalline* compound, m. p. 228—230°. Magnesium acts on a mixture of ethyl bromo*iso*butyrate and benzaldehyde, forming a neutral, crystalline *substance*, possibly  $CMe_2{<}\begin{matrix}CO{\cdot}CMe_2\\CO{-\!-\!-}O\end{matrix}{>}CHPh$, m. p. 134—135°. By substituting *p*-tolualdehyde for benzaldehyde, an analogous *substance* is produced, m. p. 138—139°. Z. K.

Reactions which Generate Organo-magnesium Compounds. Albert Reychler (*Bull. Soc. chim.*, 1906, [iii], **35**, 1079—1088. Compare Abstr., 1906, ii, 836).—Mercury ethyl and mercury phenyl do not excite a reaction between magnesium and bromobenzene in presence of ether, and scarcely affect the action of ethyl bromide on the metal. Zinc ethyl, on the contrary, induces an immediate action between magnesium and bromobenzene, especially in the proportion of 1 mol. of the exciting reagent to from 75—100 mols. of bromobenzene. This reaction is retarded and finally paralysed by the further addition of chloroform.

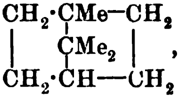
Baeyer's "active magnesium" (Abstr., 1905, i, 766) can be prepared by the careful addition of excess of metallic magnesium to a solution of iodine in ether. The solid phase (the residual magnesium) of this mixture is inactive. The liquid phase is colourless, becomes yellow on exposure to air, conducts electricity feebly, on the removal of even small quantities of the solvent by the passage of an inert gas deposits the compound $Mg(OEt_2I)_2$ (compare Zelinsky, Abstr., 1903, i, 802), and powerfully accelerates the attack of magnesium by bromobenzene.

Its action as an accelerating agent in this case is peculiar; it is very active in small quantities (1 mol. in 3000 of ether and bromobenzene), less active in medium quantity, and again more active when present in larger amount. Chloroform retards its accelerating action, and has least influence when the accelerating agent is present in the optimum quantity, and ultimately paralyses it when the number of molecules of chloroform present is 0·0015 to 0·0017 of the total number of molecules.

The accelerating action of zinc ethyl is probably indirect in the above reactions, and due to one or other of the following changes: (1) $ZnEt_2 + 2PhBr = 2EtPh + ZnBr_2$; (2) $ZnEt_2 + PhBr = EtPh + EtZnBr$. The accelerating action of Baeyer's active magnesium, or the ethereal solution of this prepared as described above, and of the exciting agents already mentioned (*loc. cit.*), is probably due to the presence of increasing quantities of substances of the type RMgX, where X is a halogen. T. A. H.

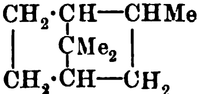
Nomenclature of Derivatives of Camphane and Fenchane. Iwan Kondakoff (*J. pr. Chem.*, 1906, [ii], **74**, 420—422).—Considering that the close relationship of camphane and fenchane and their derivatives should be expressed by the nomenclature, the author proposes to name them as derivatives of *dicyclo*heptane. The following examples are given as showing the extent to which isomerism is possible when a methyl group is introduced into the hexatomic ring of dimethyl*dicyclo*heptanes having the group $\vdots CMe_2$ in the pentatomic and hexatomic rings respectively.

The *ortho*-derivative, camphane (1 : 7 : 7-trimethyl*dicyclo*heptane),



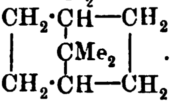
$$\begin{array}{l}CH_2\cdot CMe-CH_2\\ |\quad CMe_2\quad |\\ CH_2\cdot CH-CH_2\end{array}$$

, and the *meta*-derivative, dihydrofenchene (2 : 7 : 7-trimethyl*dicyclo*heptane),



$$\begin{array}{l}CH_2\cdot CH-CHMe\\ |\quad CMe_2\quad |\\ CH_2\cdot CH-CH_2\end{array}$$

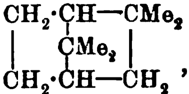
, are related to norcamphane (7 : 7-dimethyl*dicyclo*heptane),



$$\begin{array}{l}CH_2\cdot CH-CH_2\\ |\quad CMe_2\quad |\\ CH_2\cdot CH-CH_2\end{array}$$

.

To nor*iso*camphane (2 : 2-dimethyl*dicyclo*heptane),



$$\begin{array}{l}CH_2\cdot CH-CMe_2\\ |\quad CMe_2\quad |\\ CH_2\cdot CH-CH_2\end{array}$$

, are related two ortho-derivatives : 1 : 2 : 2-trimethyl- and 2 : 2 : 3-trimethyl- (*iso*camphane), two meta-derivatives: 2 : 2 : 4-trimethyl- (fenchane) and 2 : 2 : 6-trimethyl-, and one para-derivative: 2 : 2 : 5-trimethyl*dicyclo*heptane (*iso*fenchane). G. Y.

tert.-**Amylbenzene Derivatives.** Mlle. Ellen Gleditsch (*Bull. Soc. chim.*, 1906, [iii], **35**, 1094—1097. Compare Abstr., 1906, i, 942).—*tert.*-Amylbenzene, prepared by condensing *iso*amyl chloride with benzene in presence of aluminium chloride (compare Boedkter, Abstr., 1901, i, 684; Konowaloff and Egoroff, Abstr., 1899, i, 801), has b. p. 189—190°, $D_4^{21\cdot5}$ 0·8657, and n_D^{23} 1·49154. p-*Chloro*-tert.-*amylbenzene*, obtained by condensing *iso*amyl chloride with chlorobenzene in presence of aluminium chloride, is a colourless liquid with an aromatic odour, b. p. 229°, D_4^{22} 1·0070, n_D^{21} 1·59394. On nitration, it furnishes 4-*chloro*-2 : 3-*dinitro*-tert.-*amylbenzene*, which separates from boiling alcohol in small, yellow crystals, m. p. 78°.

p-*Bromo*-tert.-*amylbenzene*, similarly prepared, is a colourless liquid with an aromatic odour, b. p. 246°, D_4^{22} 1·2233, and n_D^{21} 1·53242. On nitration, it furnishes 4-*bromo*-2 : 3-*dinitro*-tert.-*amylbenzene*, which crystallises in small, yellow needles, m. p. 71°.

When chlorobenzene is treated with ethyl bromide or propyl chloride in presence of aluminium chloride, a mixture of products is obtained, which, on oxidation with chromic acid, yields both *o*- and *p*-chlorobenzoic acids, whence it appears that the comparatively light alkyl radicles, ethyl and propyl, are able, under these conditions, to enter the benzene ring both in the ortho- and para-positions.

T. A. H.

A New Mode of Formation of Phenylacetylene. GOTTFRIED MÜHLHAUSEN (*Ber.*, 1906, **39**, 4146—4147).—Phenylacetylene is formed in 10% yield when dibenzylideneacetone tetrabromide is heated with alcoholic potassium hydroxide. A. McK.

Existence of Additive Compounds of Aromatic Nitro-derivatives with Haloid Mercury Salts. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 459—466. Compare Abstr., 1905, i, 869).—The author has examined the melting-point curves of mixtures of (1) mercuric chloride with nitrobenzene, *o*-, *m*-, or *p*-nitrotoluene, *p*-nitroanisole, or *a*-nitronaphthalene, and of (2) mercuric bromide with *p*-nitrotoluene, in order to ascertain whether double compounds are formed between these pairs of salts.

The results show that the property of forming double salts with mercuric chloride is an almost general property of aromatic nitro-derivatives, which hence behave similarly to the somewhat analogously constituted iodoxy-derivatives. Unlike the compounds formed by the latter, those yielded by the nitro-derivatives are only slightly stable and in no case exhibit a definite melting point. The property of forming double salts with mercuric bromide is not general with the aromatic nitro-derivatives, and is only manifested by those substances with which mercuric chloride gives a relatively stable double salt. The nitro-compounds resemble the iodoxy-derivatives in not forming double salts with mercuric iodide. T. H. P.

Solubility of Sodium Naphthalene-β-sulphonate in Water and in Hydrochloric Acid. EMIL FISCHER (*Ber.*, 1906, **39**, 4144—4145).—The numbers 6·04, 6·47, 5·35, 4·13, and 2·42 respectively represent the number of parts of sodium naphthalene-β-sulphonate, which are described by 100 parts of water, *N*-hydrochloric acid, 2*N*-hydrochloric acid, 3*N*-hydrochloric acid, and 5*N*-hydrochloric acid respectively at 23·9°. A. McK.

Constitutional Formula of some Dimethylanthracenes. JAMES LAVAUX (*Compt. rend.*, 1906, **143**, 687—690).—Additional evidence that B-dimethylanthracene (Abstr., 1905, i, 125) is the 2 : 7-dimethylanthracene (Abstr., 1905, i, 698) is afforded by the facts (1) that β-methylanthracene is formed when the corresponding methylanthracenecarboxylic acid (obtained by reducing the methylanthraquinonecarboxylic acid with zinc and ammonia) is distilled with soda lime; (2) that a mixture of *iso*phthalic and terephthalic acids is produced when the corresponding anthraquinonedicarboxylic acid is fused with potassium hydroxide, which shows that the anthraquinonedicarboxylic acid must have been the 2 : 7- or the 2 : 6-compound. As, however, 2 : 6-dimethylanthracene has been isolated by Dewar and Jones (Trans., 1904, **85**, 217) and is distinct from B-dimethylanthracene, the latter must be the 2 : 7-isomeride.

When the methylanthracenecarboxylic acid obtained from the A-dimethylanthracene is distilled with soda lime the product is β-methylanthracene, showing that one of the methyl groups in the original hydrocarbon is in the β-position; further, when the corresponding anthraquinonedicarboxylic acid is fused with potassium hydroxide at 260° for thirteen days of twenty-four hours each, a mixture of phthalic, *iso*phthalic, and terephthalic acids is obtained, and only the 1 : 6- or the 1 : 7-isomeride would yield the three isomeric phthalic acids; the A-dimethylanthracene is therefore the 1 : 6- or the 1 : 7-isomeride. M. A. W.

Phenanthrene Series. XIX. 2 : 9 : 10-Trichlorophenanthrene and 2-Chlorophenanthraquinone. JULIUS SCHMIDT and RICHARD SCHALL (*Ber.*, 1906, **39**, 3891—3895).—2 : 9 : 10-*Trichlorophenanthrene*, $C_{14}H_7Cl_3$, is formed when phenanthrene is chlorinated in the presence of a small amount of iodine, or even better by passing chlorine into 9-bromophenanthrene heated on the water-bath and kept in sunlight. When the chlorination is incomplete, 9 : 10-dichlorophenanthrene is formed. The trichloro-derivative crystallises from alcohol in colourless needles, m. p. 123—124°. When oxidised with an aqueous acetic acid solution of chromic acid, it yields 2-*chlorophenanthraquinone*, $C_{14}H_7O_2Cl$, which crystallises from glacial acetic acid in yellowish-red needles, m. p. 235—237°. When mixed with phenanthraquinone, this melts at 190° and cannot be purified by crystallisation. The *oxime*, $C_{14}H_8O_2NCl$, forms greenish-yellow needles, m. p. 140—141°. The constitution of the chlorophenanthraquinone has been established by conversion into p-*chlorodiphenic acid*, $C_{14}H_9O_4Cl$, which has been obtained also from *p*-aminodiphenic acid by Sandmeyer's reaction. It crystallises in colourless needles, m. p. 237°. J. J. S.

Triphenylmethyl and Tervalent Carbon. Constitution of Benzopinacolin. JULIUS SCHMIDLIN (*Ber.*, 1906, **39**, 4183—4198. Compare Abstr., 1906, i, 392).—Further attempts to elucidate the constitution of triphenylmethyl. Magnesium triphenylmethyl chloride exists in two modifications. The α-form, prepared as described previously (*loc. cit.*), is not particularly stable, and by heating, alone or in benzene solution, for three hours at 80—90°, changes into the β-isomeride which exhibits the normal reactions of a Grignard reagent. The α-form, prepared in absolutely dry ether, yields about 50% each of triphenylmethyl and triphenylmethane by the action of dilute hydrochloric acid in an atmosphere of hydrogen, but the presence of a trace of moisture in the solvent causes the formation of triphenylcarbinol by the action of the mineral acid. Carbon dioxide, acting on the α-form at the moment of its production, gives triphenylacetic acid in 83% yield, but when the gas is passed into a solution, already prepared, the main product is triphenylmethyl.

A vigorous reaction ensues when benzaldehyde and α-magnesium triphenylmethyl chloride are mixed in anhydrous ethyl ether-benzene solution, the liquid becomes dark red, and γ-*benzopinacolin*, $C_{26}H_{20}O$, is obtained, m. p. 165—166°, which seems to be identical with Bourcet's *p*-benzoyltriphenylmethane, m. p. 164° (Abstr., 1897, i, 566). In the presence of moisture, a red coloration is not produced in the preceding reaction and benzoin is formed.

Both the α- and the β-modifications in ethereal solution yield triphenylmethane with cold glacial acetic acid.

The normal β-form, $MgCl\cdot CPh_3$, reacts with benzaldehyde to form β-benzopinacolin, which therefore has the constitution $CPh_3\cdot COPh$ (compare Thörner and Zincke, Abstr., 1878, 425; Wertheimer, Abstr., 1906, i, 271).

In answer to Gomberg and Cone's contention (Abstr., 1906, i, 414), the author shows that the ethereal solution of α-magnesium triphenylmethyl chloride cannot contain free triphenylmethyl, because (1) after conversion of the α- into the β-modification the solution does not contain triphenylmethyl, and (2) triphenylmethyl, by similar treatment, remains unchanged,

Since the α-form cannot contain the group $CPh_3\cdot$, the triphenylmethyl obtained from it cannot have the constitution CPh_3. C. S.

"Triphenylmethyl" and its Haloid Derivatives. Alexei E. Tschitschibabin (*J. pr. Chem.*, 1906, [ii], **74**, 340—344. Compare Abstr., 1905, i, 125, 270).—A criticism of Hantzsch's paper (Abstr., 1906, i, 617) and a claim for priority. Whilst the analogy drawn between the derivatives of triphenylmethane and trinitromethane is new, Hantzsch's experiments are insufficient to show that hexanitroethane cannot exist.

The relation of the colour of triphenylmethyl and its haloid derivatives to the structure of triphenylmethyl is discussed shortly.

G. Y.

Hexaphenylethane. Julius Schmidlin (*Ber.*, 1906, **39**, 4198—4204).—Various unsuccessful attempts to synthesise hexaphenylethane are described. The most promising result is obtained by the interaction of β-magnesium triphenylmethyl chloride and triphenylchloromethane, whereby a white, crystalline *substance* is formed, which gives analytical results approximating to the formula C_2Ph_6; this, however, has not yet been obtained free from magnesium. It sinters at 240—260°, and has m. p. 275—276°. C. S.

A New Method of Nitrating. Otto N. Witt and Alfred Utermann (*Ber.*, 1906, **39**, 3901—3905. Compare Orton, Trans., 1902, **81**, 806).—When a cold glacial acetic acid solution of acetanilide is nitrated with a cold glacial acetic acid solution of fuming nitric acid containing a small amount of carbamide, an 87% yield of mononitro-products is obtained. Three-fourths consists of the ortho- and one-fourth of the para-compound, whereas when an excess of nitric acid alone is used the chief product is the para-compound. The ortho- and para-derivatives can be separated readily by means of an aqueous alcoholic solution of potassium hydroxide in which the ortho-compound is soluble at 0°. J. J. S.

[Adipanilide]. Eyvind Bödtker (*Ber.*, 1906, **39**, 4003).—Adipanilide (Abstr., 1906, i, 827) has been prepared by Balbiano (Abstr., 1902, i, 741). C. S.

Decomposition of N : N′-Diarylmethylenediamines. CARL A. BISCHOFF and EMANUEL FRÖHLICH (*Ber.*, 1906, **39**, 3964—3981. Compare Abstr., 1903, i, 26).—*o*-Hydroxybenzylaniline and the para-isomeride occur among the products obtained by heating methylenedianiline and phenol at 200°. With resorcinol in acetone-benzene solution the base yields 1 : 3-*dihydroxybenzylaniline*,

$$C_6H_3(OH)_2\cdot CH_2\cdot NHPh,$$

m.p. 159, whilst oxanilide and *o*-hydroxybenzylaniline are obtained when methylenedianiline is heated with phenyl oxalate in xylene solution. Oxalo-*o*-toluidide is obtained from phenyl oxalate and *o*-toluidine or methylenedi-*o*-toluidine in boiling benzene.

Methylenedi-*p*-toluidine, when heated with phenol in xylene solution, yields *o*-hydroxybenzyl-*p*-toluidine (m. p. 121°); with resorcinol, a m-*dihydroxybenzyl*-p-*toluidine*, $C_6H_3(OH)_2\cdot CH_2\cdot NH\cdot C_7H_7$, is obtained, m. p. 165°, and with phenyl oxalate, oxalo-*p*-toluidide (m. p. 266°) is formed.

Methylenedi-*o*-anisidine, b. p. 160°/25 mm., yields with phenol in boiling benzene, Paal's *o*-hydroxybenzyl-*o*-anisidine (Abstr., 1903, i, 340), with phenol at 180—200°, the para-*isomeride*, $C_{14}H_{15}O_2N$, m. p. 125°, and with phenyl oxalate in boiling xylene, *oxalo*-o-*anisidide*,

$$C_{16}H_{16}O_4N_2,$$

m. p. 246°, which is obtained also from phenyl oxalate and *o*-anisidine.

p-*Anisidine phenoxide*, $C_{13}H_{14}O_2N$, m. p. 60°, forms colourless prisms.

Methylenedi-*p*-anisidine yields *o*-hydroxybenzyl-*p*-anisidine with phenol at 180° or in boiling xylene, oxalo-*p*-anisidide, $C_{16}H_{16}O_4N_2$, m. p. 260—261°, with phenyl oxalate, and 1 : 3-*dihydroxybenzyl*-p-*anisidine*, $C_6H_3(OH)_2\cdot CH_2\cdot NH\cdot C_6H_4\cdot OMe$, m. p. 149°, with resorcinol in benzene solution.

Methylenedi-*p*-phenetidine, b. p. 174°/12 mm., yields the following compounds by reactions similar to the preceding: p-*phenetidine phenoxide*, m. p. 52°; p-*hydroxybenzyl*-p-*phenetidine*, $C_{15}H_{16}O_2N$, m. p. 106°; oxalo-*p*-phenetidide, 1 : 3-*dihydroxybenzyl*-p-*phenetidine*,

$$(OH)_2C_6H_3\cdot CH_2\cdot NH\cdot C_6H_4\cdot OEt,$$

m. p. 156°.

Phenyl oxalate was also heated with the following bases: methylaniline at 200° gave a mixture of dimethyloxanilide, $C_{15}H_{16}O_2N_2$, m. p. 86°, and phenyl methyloxanilate; phenylhydrazine in boiling benzene gave oxalyldiphenylhydrazine; benzylaniline at 110—130°/50 mm., gave *phenyl benzyloxanilate*, $C_{21}H_{17}O_3N$, m. p. 93—94°; diphenylamine, when heated in a vacuum and subsequently at 180° under ordinary pressure, gave *phenyl phenyloxanilate*, $C_{20}H_{15}O_3N$, m. p., 127—128°; carbazole had no action. C. S.

Cyclic Imines. II. Attempts to Synthesise Heptamethyleneimine. JULIUS VON BRAUN and CARL MÜLLER (*Ber.*, 1906, **39**, 4110—4119. Compare Braun and Steindorff, Abstr., 1905, i, 826).—Heptamethyleneimine might be formed by elimination of ammonia from heptamethylenediamine or of the hydrogen haloid from η-chloro- or η-bromo-heptylamine. The diamine is easily prepared in large quantities by reduction of pimelonitrile (Abstr., 1905, i, 636), but the action of phosphorus pentachloride on dibenzoylheptamethylenediamine leads to the formation chiefly of αη-dichloroheptane and only of small quantities of η-chloroheptylamine (Abstr., 1905, i, 634). η-Chloro- and η-bromo-heptylamine are obtained, however, in good yields from ζ-phenoxyhexylamine through the following series of compounds.

The action of phosphorus pentachloride on benzoyl-ζ-phenoxyhexylamine (Braun and Steindorff, *loc. cit.*) leads to the formation of benzonitrile and *phenyl ζ-chlorohexyl ether*, $OPh\cdot[CH_2]_6\cdot Cl$, which forms a colourless, aromatic oil, b. p. 164—165°/11 mm., and when boiled with sodium iodide in alcoholic solution yields *phenyl ζ-iodohexyl ether*, $OPh\cdot[CH_2]_6\cdot I$. This is obtained in white crystals, m. p. 25°, b. p. 183—184°/11 mm., and forms αζ-diphenoxyhexane when heated with an excess of sodium phenoxide.

When boiled with potassium cyanide in aqueous-alcoholic solution, phenyl ζ-chlorohexyl ether reacts only slowly, but the ζ-iodo-ether more quickly and completely, forming ζ-phenoxyheptonitrile,

$$OPh\cdot[CH_2]_6\cdot CN,$$

which crystallises from light petroleum in snow-white leaflets, m. p. 32°, and on reduction with sodium and alcohol yields *η-phenoxyheptylamine*, $OPh\cdot[CH_2]_7\cdot NH_2$, m. p. 32—34°, b. p. 185°/11 mm. This is precipitated on addition of an alkali hydroxide to its acid solution, and absorbs moisture and carbon dioxide from the atmosphere; the *hydrochloride*, $OPh\cdot[CH_2]_7\cdot NH_2,HCl$, m. p. 125—127°, crystallises from water or a mixture of alcohol and ether; the *platinichloride*, $(C_{13}H_{21}ON)_2H_2PtCl_6$, commences to blacken at 200° and is melted at 210°. The *benzoyl* derivative, $OPh\cdot[CH_2]_7\cdot NHBz$, m. p. 89—90°, crystallises from alcohol; the *benzenesulphonyl* derivative,

$$OPh\cdot[CH_2]_7\cdot NH\cdot SO_2Ph,$$

m. p. 47°, crystallises from aqueous alcohol. The action of carbon dioxide on η-phenoxyheptylamine in aqueous solution in presence of a small amount of sodium hydroxide leads to the formation of the substituted *carbamate* of the amine

$$OPh\cdot[CH_2]_7\cdot NH\cdot CO_2H,NH_2\cdot[CH_2]_7\cdot OPh,$$

which separates as a delicate, white powder, m. p. 90—98°, and decomposes and evolves gas at 120°. η-Chloroheptylamine (Abstr., 1905, i, 634) is formed by heating η-phenoxyheptylamine hydrochloride with concentrated hydrochloric acid at 90° under pressure for six hours. The *picrate*, $NH_2\cdot[CH_2]_7\cdot Cl,C_6H_3O_7N_3$, forms a yellow, crystalline powder, m. p. 102—104°.

η-Bromoheptylamine, $NH_2\cdot[CH_2]_7\cdot Br$, obtained by heating the phenoxy-compound with hydrobromic acid at 80°, is isolated as the *hydrobromide*, which forms a hygroscopic, reddish-brown mass; the *picrate*, $Br\cdot[CH_2]_7\cdot NH_2,C_6H_3O_7N_3$, m. p. 100—102°. The *benzoyl* derivative, $Br\cdot[CH_2]_7\cdot NHBz$, m. p. 69°, crystallises from a mixture of ether and light petroleum. The yield of η-bromohexylamine, calculated from the benzoyl-ζ-phenoxyhexylamine, amounts to about 50°/₀ of the theoretical.

When heated with an aqueous alkali hydroxide, η-bromoheptylamine hydrobromide yields traces of a basic *substance*, which is volatile in a current of steam, has an odour resembling that of piperidine, and forms a *platinichloride* and a *product* having the empirical formula of heptamethyleneimine, $C_7H_{15}N$. This forms a wax-like mass, is not volatile with steam, is readily soluble in alcohol, chloroform, or acids, and absorbs carbon dioxide from the atmosphere. The *platinichloride*, $(C_7H_{15}N)_2,H_2PtCl_6$, is amorphous, commences to blacken at 205°, m. p. 238°, decomposing. The quaternary *iodide*, $C_7H_{14}NMe_2I$, obtained on methylation, crystallises from a mixture of ether and methyl alcohol; a stable liquid hydrosol of silver iodide is formed on addition of silver nitrate to the aqueous solution of the quaternary iodide.

η-Chloroheptylamine reacts with alkali hydroxides in the same manner as, but more slowly than, the η-bromo-base. A pure, crystalline derivative of the secondary base suitable for a molecular weight determination could not be obtained.

When heated alone, heptamethylenediamine hydrochloride decomposes into a black, carbonaceous mass, but on distillation with soda-lime, yields traces of ammonia and a colourless, basic, liquid distillate consisting chiefly of heptamethylenediamine.

These results are in agreement with the formation of only the acyclic diamine on reduction of pimelonitrile, whereas both acyclic diamines and cyclic imines are formed on reduction of the analogous ethylene and trimethylene dicyanides. G. Y.

Behaviour towards Boiling Hydriodic Acid of Alkyl Groups attached to Nitrogen. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1906, 27, 849—877. Compare Goldschmiedt and Hönigschmid, Abstr., 1903, ii, 578; 1904, i, 86; *ibid.*, ii, 94; Busch, Abstr., 1902, i, 501; Decker, Abstr., 1903, ii, 763).—The author has investigated the behaviour towards boiling hydriodic acid of forty-four substances containing the group $\vdots$NMe or $\vdots$NEt. The tabulated results show that the great majority of these lose the alkyl group as the alkyl iodide; the velocity of the reaction, however, varies considerably, depending on the structure of the nucleus and the nature and position of substituting groups, being often so small that the heating must be prolonged far past the time necessary for a methoxyl determination before a weighable quantity of silver iodide is obtained. In general, the ethyl are more stable than the methyl compounds.

Of the substances investigated, only three, diphenylmethylamine and *o*- and *p*-dimethylaminobenzaldehydes, yield methyl iodide in such manner as to simulate the presence of methoxyl groups. In most cases, the silver solution remains clear for at least an hour, and then suddenly deposits the double salt of silver iodide and nitrate (Abstr., 1904, ii, 94); in this, methyl and ethyl compounds behave similarly. On the other hand, methylanthranilic acid, dimethylanthranilic acid, anthraquinone derivatives, methylcarbazole, and pyramidone yield methyl iodide with sufficient rapidity to cause a *plus* error in the estimation of methoxyl in the analysis of a methoxy-derivative.

The influence of the benzene nucleus on the mobility of the alkyl group is shown by the behaviour of diphenylmethylamine, tetramethyldiaminodiphenylmethane, and tetramethyldiaminotriphenylmethane. The influence of the naphthalene nucleus is much greater in α- than in β-derivatives. The velocity of the formation of methyl iodide by methylaniline is increased by the introduction of negative substituting groups in the para-position, in the order Br, $CO_2H\cdot C_6H_4\cdot CO\cdot$, NO, $\cdot CO\cdot$, $\cdot CO_2H$, and $\cdot COH$. Negative substituting groups have greater influence in the para- than in the ortho-, and least in the meta-position.

In an aryldimethylamine the average stability of the methyl groups is greater than the stability of the methyl of the corresponding arylmethylamine, unless a negative substituting group is present when the relative stabilities are the converse.

It is noted that in equal periods of time, diphenylmethylamine yields four times as much methyl iodide as does the closely-related methylcarbazole. Whilst antipyrine causes no turbidity of the silver nitrate solution in six hours, its dimethylamino-derivative loses 25°/₀ of the methyl of the side chain in two hours, and on prolonged boiling not only the whole of the methyl of the dimethylamino- but also part of the methyl of the methylimino-group of the nucleus. G. Y.

Halogen Derivatives of 4-Aminodiphenyl and of 4-Aminodiphenyl-4′-oxamic Acid. P. Gelmo (*Ber.*, 1906, **39**, 4175—4183).—4-*Chloro-4′-aminodiphenyl*, $C_{12}H_{10}NCl$, obtained from Täuber's diazo-solution (Abstr., 1894, i, 597) by the Sandmeyer reaction, forms colourless leaflets, m. p. 134° (corr.). The *hydrochloride* and the *sulphate* are mentioned; the *acetyl* derivative has m. p. 245° (corr.). 4-*Bromo-4′-aminodiphenyl* forms yellow leaflets, m. p. 145° (corr.); the *acetyl* derivative has m. p. 247° (corr.). 4-*Iodo-4′-aminodiphenyl* forms yellow leaflets, m. p. 166° (corr.); the *acetyl* derivative has m. p. 250° (corr.).

Diazotised benzidineoxamic acid forms an orange-yellow, crystalline mass which decomposes at 110°. From it the following substances are prepared in the usual way. 4-*Hydroxydiphenyl-4′-oxamic acid*, $C_{14}H_{11}O_4N$, decomposes above 270°, and by hydrolysis yields 4-amino-4′-hydroxydiphenyl. 4-*Chlorodiphenyl-4′-oxamic acid* forms yellowish-white needles and decomposes at 213°; the *ammonium* salt decomposes at 247°. The corresponding *bromo*-compound and its *ammonium* salt decompose at 240° and 260° respectively, the *iodo*-compound and its *ammonium* salt at 280° and 290° respectively. By hydrolysis these oxamic acids yield the compounds mentioned previously. C. S.

Methylpicramic Acid. Walther Borsche and Arnold Heyde (*Ber.*, 1906, **39**, 4092—4093. Compare Abstr., 1906, i, 15).—As *o*-nitrophenols having a hydrogen atom in the ortho-position to the nitro-group yield purpurates when treated with potassium cyanide, methylpicramic acid must be 2:6-dinitro-4-amino-*m*-cresol, and not 2:4-dinitro-6-amino- or 4:6-dinitro-2-amino-*m*-cresol, since, when heated with potassium cyanide in aqueous solution on the water-bath, it forms potassium methylpicramate and not a methylpicramopurpurate, hydrogen cyanide being liberated. G. Y.

Action of Phosphorus Pentabromide and Pentachloride on Phenyl Alkyl Ethers. Wilhelm Autenrieth and Paul Mühlinghaus (*Ber.*, 1906, **39**, 4098—4106. Compare Autenrieth, Abstr., 1895, i, 511; Bachmann, Abstr., 1883, 726).—Phosphorus pentabromide or pentachloride reacts with phenyl alkyl ethers at the laboratory temperature or when gently heated on the water-bath, according to the equation $C_6H_5{\cdot}OR + PX_5 = C_6H_4X{\cdot}OR + PX_3 + HX$. The reaction has been extended to a number of ethers of substituted phenols, some of which require prolonged heating on the water-bath, and to alkyl naphthoxides, which enter readily into the reaction.

Phenetole and phosphorus pentabromide form *p*-bromophenetole, b. p. 225—226° (233°, Lippmann, *Jahresber.*, 1870, 548), which, when heated with fuming hydrochloric acid at 180° under pressure, is hydrolysed, forming *p*-bromophenol, b. p. 235—236°.

A molecular mixture of anisole and phosphorus pentabromide yields *p*-bromoanisole, C_7H_7OBr, b. p. 213—216°, in a 90% yield. When heated with fuming hydrochloric acid this forms *p*-bromophenol, which is identified by conversion into its benzoyl derivative. The action of 2 mols. of phosphorus pentabromide on 1 mol. of anisole leads to the formation of 2 : 4-dibromoanisole in an almost theoretical yield.

2 : 4-*Dibromophenetole*, $C_6H_3Br_2{\cdot}OEt$, formed by heating *p*-bromophenetole with phosphorus pentabromide on the water-bath, crystallises from alcohol in large, rhombic plates, m. p. 50°, and has a disagreeable odour of fennel.

A molecular mixture of phenetole and phosphorus pentachloride yields *p*-chlorophenetole, m. p. 212—214° (210—212°, Beilstein and Kurbatoff, *Annalen*, 1875, **176**, 30), which reacts only slowly with a second mol. of phosphorus pentachloride, forming probably 2 : 4-dichlorophenetole.

p-Tolyl ethyl ether and phosphorus pentabromide form *bromo*-p-*tolyl ethyl ether*, $C_6H_3BrMe{\cdot}OEt$ [Me : Br : OEt = 1 : 3 (?) : 4], which is obtained as a colourless liquid, b. p. 239—240°.

The action of phosphorus pentachloride on *p*-tolyl ethyl ether at 40° leads to the formation of (*a*) 3-*chloro*-p-*tolyl ethyl ether*, $C_6H_3ClMe{\cdot}OEt$, which forms a colourless, mobile liquid having a pleasant odour, b. p. 133—138°/26 mm. or 233—238°/760 mm., and when heated with fuming hydrochloric acid yields 3-chloro-*p*-cresol, and (*b*) 3 : 5-*dichloro*-p-*tolyl ethyl ether*, $C_6H_2Cl_2Me{\cdot}OEt$ [Me : Cl_2 : OEt = 1 : 3 : 5 : 4], b. p. 147—154°/26 mm., which on hydrolysis yields 3 : 5-dichloro-*p*-cresol.

1-*Bromo*-β-*naphthyl methyl ether*, $C_{10}H_6Br{\cdot}OMe$, formed by the action of phosphorus pentabromide on β-naphthyl methyl ether, crystallises in glistening, white leaflets, m. p. 84—85°. 4-*Bromo*-1-*naphthyl ethyl ether*, $C_{10}H_6Br{\cdot}OEt$, formed in the same manner from α-naphthyl ethyl ether, crystallises in white prisms, m. p. 48°.

The action of phosphorus pentachloride on α-naphthyl ethyl ether leads to the formation of two *products*, b. p. 302—306°, decomposing slightly, and 360° respectively. G. Y.

Formation of Chains. LXVI. Reactions of Phenyl and Tolyl Esters of α-Bromo-fatty Acids with Sodium Phenoxide and Tolyloxide.

CARL A. BISCHOFF (*Ber.*, 1906, **39**, 3830—3839. Compare Abstr., 1905, i, 157).—The products of the reaction $R{\cdot}O{\cdot}Na + CR''R'''Br{\cdot}CO_2R = R{\cdot}O{\cdot}CR''R'''{\cdot}CO_2R + NaBr$, in which R = phenyl, the three tolyls, carvacryl, thymyl, guaiacyl, the naphthyls, and the three nitrophenyls are described in this and the three following abstracts. The aryl esters of the bromo-fatty acids are prepared by the action of the acid bromides on the phenols or their sodium salts. The formation of the aryl ester of the α-aryloxy-fatty acid takes place with 78—90°/₀ yields on boiling the α-bromo-ester with the sodium aryl oxide in xylene solution for twenty hours.

[With W. WACHSMUTH.]—*Phenyl α-bromopropionate*, $CHMeBr\cdot CO_2Ph$, is a colourless oil, b. p. 126°/12 mm., 153°/34 mm., or 248—249°/765 mm., D_{15}^{15} 1·412. *Phenyl α-bromobutyrate*, $C_{10}H_{11}O_2Br$, b. p. 157°/31 mm. or 263—264°/765 mm., D_{15}^{15} 1·373. *Phenyl α-bromo*iso*butyrate* is obtained as a fuming, yellow oil, b. p. 157°/42 mm., decomposes at 248°/765 mm., D_{15}^{15} 1·366. *Phenyl α bromo*iso*valerate*, $C_{11}H_{13}O_2Br$, forms a colourless oil, b. p. 183°/33 mm., D_{15}^{15} 1·315; when boiled in air, it becomes yellow and evolves hydrogen bromide.

Phenyl α-phenoxypropionate, $OPh\cdot CHMe\cdot CO_2Ph$, crystallises from methyl alcohol in needles, m. p. 52°, b. p. 190°/18 mm., D_{15}^{15} 1·147; it distils and decomposes slightly above 300°/760 mm., yielding a colourless oil. *Phenyl α-phenoxybutyrate*, $C_{16}H_{16}O_3$, crystallises from methyl alcohol in prisms, m. p. 48—49°, b. p. 202—203°/25 mm., D_{15}^{15} 1·136. *Phenyl α-phenoxy*iso*butyrate* crystallises in white needles, m. p. 24—26°, b. p. 194—195°/16 mm. *Phenyl α-phenoxy*iso*valerate*, $C_{17}H_{18}O_3$, crystallises from light petroleum in stout, colourless, rhombic plates, m. p. 44°, b. p. 196—197°/26 mm.

A table is given showing the weights and boiling points of the fractions obtained on distilling the crude phenyl α-phenoxy-esters.

[With J. BIHMANN.]—o-*Tolyl α-bromopropionate*, $CHMeBr\cdot CO\cdot O\cdot C_7H_7$, b. p. 139°/12 mm. o-*Tolyl α-bromobutyrate*, $C_{11}H_{13}O_2Br$, b. p. 139·5°/12 mm. o-*Tolyl α-bromo*iso*butyrate*, b. p. 127·5°/12 mm., D_{15}^{15} 1·332. o-*Tolyl α-bromo*iso*valerate*, $C_{12}H_{15}O_2Br$, b. p. 143°/12 mm., D_{15}^{15} 1·296. When distilled under atmospheric pressure, the *o*-tolyl α-bromo-esters decompose, evolving hydrogen bromide.

o-*Tolyl α-*o*-tolyloxypropionate*, $C_{17}H_{18}O_3$, forms a light yellow oil, b. p. 188°/13 mm., D_{15}^{15} 1·103. o-*Tolyl α-*o*-tolyloxybutyrate*, $C_{18}H_{20}O_3$, is obtained as a slightly yellow oil, b. p. 189°/12 mm., D_{15}^{15} 1·091. o-*Tolyl α-*o*-tolyloxy*iso*butyrate* forms a light yellow oil, b. p. 185°/11 mm., D_{15}^{15} 1·092. o-*Tolyl α-*o*-tolyloxy*iso*valerate*, $C_{19}H_{22}O_3$, forms a light yellow oil, b. p. 191°/15 mm., D_{15}^{15} 1·073.

[With K. SMOLNIKOFF.]—m-*Tolyl α-bromopropionate*, b. p. 137·5°/12 mm. m-*Tolyl α-bromobutyrate* forms a slightly yellow oil, b. p. 144°/12 mm. m-*Tolyl α-bromo*iso*butyrate*, a light yellow oil, b. p. 134°/12 mm. m-*Tolyl α-bromo*iso*valerate*, a light yellow oil, b. p. 150°/12 mm.

m-*Tolyl α-*m*-tolyloxypropionate* forms a slightly yellow oil, b. p. 199°/15 mm. m-*Tolyl α-*m*-tolyloxybutyrate*, b. p. 202°/15 mm. m-*Tolyl α-*m*-tolyloxy*iso*butyrate*, b. p. 201°/15 mm. m-*Tolyl α-*m*-tolyloxy*iso*valerate*, b. p. 202°/15 mm.

[With A. GUSSEW.]—p-*Tolyl α-bromopropionate*, b. p. 137°/12 mm. p-*Tolyl α-bromobutyrate*, b. p. 148·5°/12 mm. p-*Tolyl α-bromo*iso*butyrate* crystallises from light petroleum in pyramids, m. p. 39°, b. p. 135·2°/12 mm. p-*Tolyl α-bromo*iso*valerate*, b. p. 154·5°/12 mm.

p-*Tolyl α*-p-*tolyloxypropionate* crystallises in small, nodular aggregates of colourless needles, m. p. 90°, b. p. 200°/15 mm. p-*Tolyl α*-p-*tolyloxybutyrate*, b. p. 203°/15 mm. p-*Tolyl α*-p-*tolyloxy*iso*butyrate*, b. p. 197°/15 mm. p-*Tolyl α*-p-*tolyloxy*iso*valerate* forms a colourless, viscid oil, b. p. 215°/15 mm. G. Y.

Formation of Chains. LXVII. Reactions of Carvacryl and Thymyl Esters of α-Bromo-fatty Acids with Sodium Carvacryl and Thymyl Oxides. CARL A. BISCHOFF (*Ber.*, 1906, **39**, 3840—3846. Compare preceding abstract).—[with A. BLUMENTHAL.]—*Carvacryl α-bromopropionate*, $C_{13}H_{17}O_2Br$, b. p. 157°/12 mm. *Carvacryl α-bromobutyrate*, $C_{14}H_{19}O_2Br$, b. p. 163°/12 mm. *Carvacryl α-bromo*iso*butyrate*, b. p. 155·5°/12 mm. *Carvacryl α-bromo*iso*valerate*, $C_{15}H_{21}O_2Br$, b. p. 172·5°/12 mm. These four esters are formed only by the action of the acid bromides on sodium carvacryl oxide.

Carvacryl α-carvacryloxypropionate, $C_{23}H_{30}O_3$, crystallises in colourless prisms, m. p. 39°, b. p. 220°/15 mm. *Carvacryl α-carvacryloxybutyrate*, $C_{24}H_{32}O_3$, forms a colourless oil, b. p. 226°/15 mm. *Carvacryl α-carvacryloxy*iso*butyrate* is obtained as a colourless oil, b. p. 219°/15 mm. *Carvacryl α-carvacryloxy*iso*valerate*, $C_{25}H_{34}O_3$, a colourless oil, b. p. 227°/15 mm.

A table is given showing the boiling points and weights of the fractions obtained on distilling the four crude carvacryl α-carvacryloxy-esters.

[With K. KOWERSKI.]—*Thymyl α-bromopropionate*, $C_{13}H_{17}O_2Br$, forms a colourless oil, b. p. 155°/12 mm. *Thymyl α-bromobutyrate*, $C_{14}H_{19}O_2Br$, is obtained as a colourless oil, b. p. 162°/12 mm. *Thymyl α-bromo*iso*butyrate*, a colourless oil, b. p. 151°/12 mm. *Thymyl α-bromo*iso*valerate*, $C_{15}H_{21}O_2Br$, a colourless oil, b. p. 166°/12 mm. These four esters are formed by the action of the acid bromides on thymol.

Thymyl α-thymoxypropionate, $C_{23}H_{30}O_3$, forms a yellow, viscid liquid, b. p. 217°/15 mm. *Thymyl α-thymoxybutyrate*, $C_{24}H_{32}O_3$, forms a light-yellow, viscid oil, b. p. 222·5°/15 mm. *Thymyl α-thymoxy*iso*butyrate* is obtained as a light yellow, viscid oil, b. p. 218°/15 mm. *Thymyl α-thymoxy*iso*valerate*, $C_{25}H_{34}O_3$, a light yellow, viscid oil, b. p. 221·5°/15 mm. G. Y.

Formation of Chains. LXVIII. Reactions of Naphthyl and Guaiacyl Esters of α-Bromo-fatty Acids with Sodium Naphthoxides and Guaiacyl Oxide. CARL A. BISCHOFF (*Ber.*, 1906, **39**, 3846—3854. Compare preceding abstracts).—[With M. GUSSEW.]—Of the α-naphthyl esters of the α-bromo-fatty acids only the α-bromo*iso*valerate can be prepared in a state of purity by the action of the acid bromide on α-naphthol; the lower homologues are prepared from sodium α-naphthoxide.

α-*Naphthyl α-bromopropionate*, $C_{13}H_{11}O_2Br$, forms a light yellow, viscid oil, b. p. 190°/15 mm. (corr.). α-*Naphthyl α-bromobutyrate*, $C_{14}H_{13}O_2Br$, a light yellow, viscid oil, b. p. 198°/15 mm. (corr.). α-*Naphthyl α-bromo*iso*butyrate*, a light yellow, viscid oil, b. p.

186·5°/15 mm. (corr.), decomposing. *α-Naphthyl α-bromo*iso*valerate*, $C_{15}H_{15}O_2Br$, crystallises in colourless leaflets, m. p. 68°.

α-Naphthyl α-α-naphthoxypropionate, $C_{23}H_{18}O_3$, crystallises from glacial acetic acid, m. p. 94—96°. *α-Naphthyl α-α-naphthoxybutyrate*, $C_{24}H_{20}O_3$, crystallises in leaflets, m. p. 96°. α-Naphthyl α-bromo*iso*butyrate and α-bromo*iso*valerate react with sodium α-naphthoxide, forming 91 and 85 °/₀ of sodium bromide respectively, but the organic products could not be purified.

[With A. Willums.]—*β-Naphthyl α-bromopropionate* crystallises in nodular aggregates, m. p. 74°, b. p. 194°/15 mm. *β-Naphthyl α-bromobutyrate*, $C_{14}H_{13}O_2Br$, crystallises from light petroleum in colourless leaflets, m. p. 54°, b. p. 202°/15 mm. *β-Naphthyl α-bromo*iso*butyrate* crystallises from light petroleum in colourless leaflets, m. p. 97—98°, b. p. 185°/15 mm. *β-Naphthyl α-bromo*iso*valerate* forms heavy, crystalline masses, m. p. 51°, b. p. 205°/15 mm.

β-Naphthyl α-β-naphthoxypropionate crystallises in slender needles, m. p. 95—96°. *β-Naphthyl α-β-naphthoxybutyrate* crystallises from glacial acetic in leaflets, m. p. 80—82°. *β-Naphthyl α-β-naphthoxy*iso*butyrate* crystallises in stout needles, m. p. 100°. *β-Naphthyl α-β-naphthoxy*iso*valerate* crystallises in stout, prismatic needles, m. p. 106°.

[With J. Wielowieyski.]—*Guaiacyl α-bromopropionate*,

$$CHMeBr{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}OMe,$$

forms a light yellow oil, b. p. 153°/12 mm. *Guaiacyl α-bromobutyrate*, $C_{11}H_{13}O_3Br$, is obtained as a colourless oil, b. p. 159°/15 mm. *Guaiacyl α-bromo*iso*butyrate*, $C_{11}H_{13}O_3Br$, a colourless, viscid oil, b. p. 149·5°/12 mm. *Guiacyl α-bromo*iso*valerate*, $C_{12}H_{15}O_3Br$, crystallises from light petroleum in monoclinic prisms, m. p. 69°, b. p. 165—165·3°/12 mm.

Guaiacyl α-guaiacyloxypropionate, $C_{17}H_{18}O_5$, crystallises from dilute alcohol, m. p. 64°, b. p. 226°/15 mm. (corr.). *Guaiacyl α-guaiacyloxybutyrate*, $C_{18}H_{20}O_5$, forms a colourless, very viscid oil, b. p. 231°/15 mm. (corr.). *Guaiacyl α-guaiacyloxy*iso*butyrate* forms a colourless, viscid oil, b. p. 221°/15 mm. (corr.). *Guaiacyl α-guaiacyloxy*iso*valerate*, $C_{19}H_{22}O_5$, b. p. 259—262°/25 mm. or 230°/15 mm. (corr.). Free guaiacol is formed in the preparation of this ester. G. Y.

Formation of Chains. LXIX. Nitrophenyl Esters of α-Bromo-fatty Acids. Carl A. Bischoff (*Ber.*, 1906, **39**, 3854—3861. Compare preceding abstracts; Bischoff and Walden, Abstr., 1894, i, 403; Bischoff, Abstr., 1900, i, 442; 1901, i, 525).—Whilst phenyl α-bromopropionate and α-bromo*iso*butyrate when boiled with sodium phenoxide in xylene solution for ten hours form 76°/₀ and 83°/₀ of the calculated amounts of sodium bromide respectively, only 1·2°/₀ of sodium bromide is formed when these esters are boiled with sodium *o*-nitrophenoxide in xylene solution for sixty-seven hours. When boiled with sodium phenoxide in xylene solution, *o*-nitrophenyl α-bromopropionate does not form sodium bromide in thirty hours; *p*-nitrophenyl α-bromopropionate forms 14°/₀ of the calculated sodium bromide in four hours, and *p*-nitrophenyl α-bromo*iso*butyrate 12°/₀ in fifteen hours; in these cases the nitrophenyl is substituted by the phenyl group. *o*-Nitrophenyl α-bromopropionate and sodium phenoxide when shaken in benzene solution react, forming phenyl α-bromopropionate, which is formed also from *p*-nitrophenyl α-bromopropionate and sodium phenoxide.

Sodium *o*-nitrophenoxide does not react with thymyl α-bromopropionate or *o*-nitrophenyl α-bromopropionate; sodium *p*-nitrophenoxide does not react with the four *p*-nitrophenyl α-bromo-fatty esters. Sodium *m*-nitrophenoxide, on the other hand, reacts with *m*-nitrophenyl α-bromopropionate in thirty hours to the extent of 74%.

[With SCHMÄHLING.]—o-*Nitrophenyl α-bromopropionate*,

$$CHMeBr\cdot CO\cdot O\cdot C_6H_4\cdot NO_2,$$

crystallises from light petroleum in white needles, m. p. 48°, b. p. 188°/12 mm. (corr.); when heated in contact with air, it becomes brown, and decomposes at 220°. o-*Nitrophenyl α-bromobutyrate*, $C_{10}H_{10}O_4NBr$, forms a light yellow oil, b. p. 187°/10 mm. (corr.). o-*Nitrophenyl α-bromo*iso*butyrate*, b. p. 183—184°/12 mm. o-*Nitrophenyl α-bromo*iso*valerate*, b. p. 190°/12 mm. These four esters are prepared by the action of the acid bromides on sodium *o*-nitrophenoxide in boiling benzene solution.

o-*Nitrophenyl α-*o*-nitrophenoxypropionate*,

$$NO_2\cdot C_6H_4\cdot O\cdot CHMe\cdot CO\cdot O\cdot C_6H_4\cdot NO_2,$$

is prepared from α-*o*-nitrophenoxypropionic acid by the action of phosphorus pentachloride, and treatment of the resulting *acid chloride* with sodium *o*-nitrophenoxide in boiling benzene solution; it crystallises in sheaves of yellow needles or microscopic prisms, m. p. 137°.

m-*Nitrophenyl α-bromopropionate*, prepared by the action of the acid bromide on sodium *m*-nitrophenoxide, b. p. 245°/120 mm., fumes on exposure to air, and absorbs moisture, forming *m*-nitrophenol and α-bromopropionic acid.

m-*Nitrophenyl α-*m*-nitrophenoxypropionate*, formed by the action of *m*-nitrophenyl α-bromopropionate or of α-bromopropionyl bromide on sodium *m*-nitrophenoxide in boiling xylene solution, crystallises from methyl alcohol, m. p. 109—110°; evaporation of the methyl alcoholic filtrate leads to the formation of *m*-nitrophenol and *methyl α-*m*-nitrophenoxypropionate*, $C_{10}H_{11}O_5N$, b. p. 173—175°/20 mm.

m-*Nitrophenyl α-bromobutyrate* forms an unstable, fuming, yellowish-brown oil, b. p. 247°/100 mm. m-*Nitrophenyl α-bromo*iso*butyrate* crystallises from light petroleum in long, yellow needles, m. p. 90—91°. m-*Nitrophenyl α-bromo*iso*valerate* forms an unstable, light yellow oil, b. p. 248°/98 mm.

[With AMBARDANOFF.]—p-*Nitrophenyl α-bromopropionate* crystallises from a mixture of alcohol and light petroleum in needles and plates, or from concentrated solutions in plates and prisms, m. p. 42—46°. p-*Nitrophenyl α-bromobutyrate* crystallises from alcohol in prisms, m. p. 48—49°. p-*Nitrophenyl α-bromo*iso*butyrate* crystallises from light petroleum in plates and prisms, m. p. 79—80°. p-*Nitrophenyl α-bromo*iso*valerate* crystallises in plates, m. p. 42—43°.

p-*Nitrophenyl α-*p*-nitrophenoxypropionate* is prepared from α-*p*-nitrophenoxypropionic acid by conversion of this into its *chloride*, which is then boiled with sodium *p*-nitrophenoxide in benzene solution. It crystallises from alcohol in microscopic rhombohedra, m. p. 137°, and is soluble in the ordinary organic solvents. G. Y.

Nitration of 4-Benzoylaminophenyl Acetate and of 4-Acetylaminophenyl Benzoate. FRÉDÉRIC REVERDIN [with L. CUISINIER] (*Ber.*, 1906, **39**, 3793—3797. Compare Reverdin and Dresel, Abstr., 1905, i, 54, 430; Reverdin and Delétra, Abstr., 1906, i, 165; Reverdin and Bucky, *ibid.*, 748).—It is found that of the diacetyl-dibenzoyl and acetyl-benzoyl derivatives of *p*-aminophenol, 4-acetylaminophenyl benzoate alone does not yield a dinitro-derivative containing both nitro-groups in the phenol nucleus. Even when more concentrated nitric acid or a mixture of nitric and sulphuric acids is used only a mononitro-derivative is formed.

4-*Benzoylaminophenyl acetate*, $NHBz\cdot C_6H_4\cdot OAc$, prepared by heating 4-benzoylaminophenol with acetic anhydride at 120°, finally with addition of a small amount of concentrated sulphuric acid, crystallises in white leaflets, m. p. 171°.

4-*Acetylaminophenyl benzoate*, $NHAc\cdot C_6H_4\cdot OBz$, prepared by shaking 4-acetylaminophenol with benzoyl chloride in aqueous sodium carbonate solution, crystallises in white needles, m. p. 171°. A mixture of this with the preceding substance melts at 155°.

Treatment of benzoylaminophenyl acetate with nitric and sulphuric acids at $-8°$, and finally at 40°, leads to the hydrolysis of the acetyl group, and consequently to the formation of 2:6-dinitro-4-benzoylaminophenol, which is formed also by direct nitration of 4-benzoylaminophenol. 3:5-*Dinitro-4-benzoylaminophenyl acetate*, $C_{15}H_{11}O_7N_3$, is formed from 4-benzoylaminophenyl acetate by nitration with a mixture of sulphuric and nitric acids in acetic anhydride under 0°, and finally at 30°, or in an impure state by nitration with nitric acid, D 1·5 at $-10°$ to $-5°$; it crystallises from alcohol in slender, white needles, m. p. 215°.

3-*Nitro-4-acetylaminophenyl* m-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot C_6H_3(NO_2)\cdot NHAc,$$

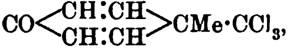
is formed together with 2:6-dinitro-4-acetylaminophenol by the action of nitric and sulphuric acids on 4-acetylaminophenyl benzoate, the final temperature not exceeding 17°. It is formed also by nitration of 4-acetylaminophenyl benzoate with nitric acid alone, or with a mixture of nitric and sulphuric acids in presence of acetic anhydride. It crystallises in slender, yellow needles, m. p. 184°, and on hydrolysis with boiling sulphuric acid yields *m*-nitrobenzoic acid and 3-nitro-4-aminophenol. G. Y.

Action of Carbon Tetrachloride and Aluminium Chloride on *p*-Cresol and its Derivatives. THEODOR ZINCKE and R. SUHL (*Ber.*, 1906, **39**, 4148—4153).—3:5-*Dichloro*-2:6-*dibromo*-p-*cresol*, obtained by brominating 3:5-dichloro-*p*-cresol in carbon tetrachloride in the presence of iron, forms white needles, m. p. 196°, and is converted by nitric acid into a *quinonitrole* and a *ψ-quinol*; the latter forms yellow needles, has m. p. 197°, and is converted by alcoholic hydrogen chloride into a tetrachloroquinone.

3:5-*Dichloro*-2:6-*dibromo*-p-*tolyl carbonate*, $(C_6MeCl_2Br_2)_2CO_3$, obtained from the dichlorodibromo-*p*-cresol and aluminium chloride in carbon tetrachloride, is a white, crystalline powder, m. p. >275°, yields dichlorodibromo-*p*-cresol with fused potassium hydroxide, carbanilides with primary aromatic amines, and carbamic acid derivatives with secondary amines; the *substance*, $NPhMe\cdot CO_2\cdot C_6MeCl_2Br_2$, obtained from methylaniline, forms white needles, m. p. 162°; the *ethyl* compound, $NPhEt\cdot CO_2\cdot C_6MeCl_2Br_2$, has m. p. 172°.

Tetrabromo-p-*tolyl carbonate*, $(C_6MeBr_4)_2CO_3$, m. p. $>330°$, is obtained from *p*-cresol, aluminium, and bromine in carbon tetrachloride, and resembles the preceding carbonate.

1-*Methyl*-1-*trichloromethyl*-4-*ketodihydrobenzene*,



$$CO<\begin{matrix}CH:CH\\CH:CH\end{matrix}>CMe\cdot CCl_3,$$

obtained from aluminium chloride and *p*-cresol in carbon tetrachloride, forms large prisms, m. p. 105°, and is volatile with steam. The ketone is converted by warm concentrated sulphuric acid into hydrogen chloride, carbonyl chloride, and cresolsulphonic acid, by nitric acid into dinitro-*p*-cresol, by alcohol and hydrochloric acid into *p*-cresol, by hydroxylamine into the *oxime*, $C_8H_8ONCl_3$, m. p. 134° (which yields an *acetyl* derivative, m. p. 85—86°), and by phenylhydrazine into the *phenylhydrazone*, $C_{14}H_{13}N_2Cl_3$, which forms yellow needles and darkens at 95° and has m. p. 130°, decomposing. C S.

Phenylation of Phenols. FRITZ ULLMANN and PAUL SPONAGEL (*Annalen*, 1906, **350**, 83—107. Compare Abstr., 1905, i, 644).—In the reaction between an alkali phenoxide and a phenyl halide in the presence of copper as a catalyst, chlorobenzene reacts most slowly and iodobenzene most rapidly, the yield in the latter case being about the same as with bromobenzene. With potassium phenoxide the yields of ether are 25, 78·2, and 91·5°/₀ respectively; by the use of sodium phenoxide the yield with bromobenzene is only 33°/₀.

The following ethers have been prepared from bromobenzene: *phenyl* o-*tolyl ether*, b. p. 267°/738·5 mm., m. p. 21·5—22°, yield 77°/₀; *phenyl* m-*tolyl ether*, b. p. 274·5°/738 mm., yield 81·1°/₀; *phenyl* p-*tolyl ether*, b. p. 277—278°/745·5 mm., yield 69·1°/₀; *phenyl thymyl ether*, b. p. 176°/25 mm., 297°/766 mm., D^{15} 1·0113; *phenyl α-naphthyl ether*, m. p. 54°, yield 40°/₀. The same ether is obtained from α-bromonaphthalene and phenol in 71·7°/₀ yield. Phenyl β-naphthyl ether, b. p. 335·5°/753 mm., m. p. 45° (compare Hönigschmid, Abstr., 1903, i, 165).

From α-bromonaphthalene have been obtained *αα'*-dinaphthyl ether and *αβ'-dinaphthyl ether*, the latter having b. p. 264°/15 mm., m. p. 81°, and forming a *picrate*, $C_{20}H_{14}O,2C_6H_3O_7N_3$, which crystallises in orange-yellow needles and has m. p. 121—122°.

Of the dibromobenzenes, the para-isomeride is the most reactive. *Catechyl diphenyl ether*, m. p. 93°, is obtained in 80·6°/₀ yield from phenol and *o*-dibromobenzene; *resorcyl diphenyl ether*, m. p. 61·5°; *quinol diphenyl ether*, m. p. 77°, b. p. 371—372°/720 mm. (compare Häussermann and Müller, Abstr., 1901, i, 382).

An excess of the cresols must be used to obtain good yields of the three following compounds from *p*-dibromobenzene: *quinol* o-*ditolyl ether*, m. p. 51°, b. p. 243°/18 mm.; quinol *m*-ditolyl ether, m. p. 57°, b. p. 253°/23 mm., whilst the corresponding *isomeride* from *p*-cresol has m. p. 102—103°

Hoffmeister's dibromophenyl ether (*Annalen*, 1872, **159**, 200) condenses with phenol to form *diphenoxydiphenyl ether*, $O(C_6H_4{\cdot}OPh)_2$, which probably has the para-constitution; it has m. p. 111° and the yield is 89 %.

m-*Aminodiphenyl ether*, obtained from *m*-bromoaniline and phenol, or by the reduction of the *m*-nitrodiphenyl ether described previously (*loc. cit.*), separates from light petroleum in large prisms, m. p. 37°, b. p. 190—191°/14 mm., and forms a *hydrochloride*, m. p. 139°, a *sulphate*, m. p. 187—189°, and an *acetyl* derivative, m. p. 83°.

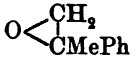
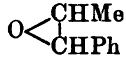
p-Aminodiphenyl ether must be prepared in an atmosphere of hydrogen to prevent the formation of coloured by-products.

o-Phenoxybenzoic acid, obtained from bromobenzene and salicylic acid, cannot be separated from the unchanged acid; it is therefore converted into xanthone, which is obtained in 21 % yield.

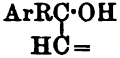
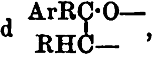
Small quantities of diphenyl ether and phenol are obtained by the prolonged heating of bromobenzene, potassium, alcohol, and copper under pressure at 150°. C. S.

Migration of the Phenyl Group; "Residual Valency" Structure of Intermediate Compounds. MARC TIFFENEAU (*Compt. rend.*, 1906, **143**, 684—687. Compare Abstr., 1902, i, 666; 1904, i, 63, 133; Abstr., 1906, i, 662, 965).—A theoretical paper in which the author discusses four possible formulæ for the unstable intermediate compounds which are formed by the elimination of hydrogen iodide from the iodohydrins of ethylenic hydrocarbons of the types

$ArRC{:}CHR'$

and $ArCH{:}CRR'$, which by an intramolecular rearrangement involving the migration of a phenyl radicle are converted into the isomeric aldehyde or ketone. The ethylene oxide formula is untenable because in certain cases these oxides have been prepared and they are stable compounds, and are converted into the isomeric ketone or aldehyde without the migration of the phenyl group, thus  $O<\begin{array}{l}CH_2\\ |\\ CMePh\end{array}$ $\longrightarrow$ $CHMePh{\cdot}CHO$ and  $O<\begin{array}{l}CHMe\\ |\\ CHPh\end{array}$ $\longrightarrow$ $CH_2Ph{\cdot}CO{\cdot}CH_3$ (Abstr., 1905, i, 523, 591). The unstable compounds cannot be regarded as homologues of vinyl alcohol because iodohydrins of the type

$OH{\cdot}CRAr{\cdot}CHIR'$

could not form such a compound by elimination of HI. The most probable structure therefore of the unstable intermediate compound is one in which a carbon atom or an oxygen and a carbon atom exhibit "residual valencies," and of the two possible formulæ based on this assumption,  $\begin{array}{l}ArRC{\cdot}OH\\ \quad |\\ \;\;HC=\end{array}$ and  $\begin{array}{l}ArRC{\cdot}O—\\ \quad\;\; |\\ \;RHC—\end{array}$, the former is untenable in the case of the iodohydrin of phenylmethylpropylene,

$OH{\cdot}CHPh{\cdot}CMe_2I$,

and other compounds, whilst the latter affords a satisfactory explanation of the formation of an ethylene oxide or a ketone according as the residual valency of the oxygen atom is orientated towards the neighbouring unsaturated carbon atom, or towards the carbon atom with which it is associated. M. A. W.

Influence of the Carbon Double-linking on the Colour of Azomethine Compounds. RICHARD MÖHLAU and RICHARD ADAM (*Zeit. Farb. Ind.*, 1906, 5, 377—383 and 402—412).—The authors give an extensive summary of previous work on the connexion between colour and constitution, adopting as their standpoint the conception of chromophorous groupings. They have investigated experimentally the influence of the $-C⁚N-$ group on the production of colour, by preparing the following compounds by combining certain aldehydes with different amines or aminophenols.

1-*Benzylideneamino-β-naphthol*, $CHPh⁚N\cdot C_{10}H_6\cdot OH$, prepared by condensing benzaldehyde with 1-amino-β-naphthol, crystallises from a mixture of chloroform and light petroleum in sheaves of bright yellow needles, m. p. 129°. *Benzylideneaminosalicylic acid*,

$$[⁚N : OH : CO_2H = 5 : 2 : 1],$$

prepared from the corresponding aminosalicylic acid, forms bright yellow needles, and is insoluble in all solvents; m. p. 256°. 4-*Cinnamylideneamino-α-naphthol*, $CHPh⁚CH\cdot CH⁚N\cdot C_{10}H_6\cdot OH$, prepared from cinnamaldehyde and 4-amino-α-naphthol in light petroleum, crystallises from acetone in lustrous yellow needles, m. p. 187°. 1-*Cinnamylideneamino-β-naphthol* crystallises from light petroleum in dark yellow, felted needles, m. p. 128°. *Cinnamylideneaminosalicylic acid*,

$$[CH⁚N : OH : CO_2H = 5 : 2 : 1],$$

crystallises from a mixture of alcohol and chloroform in dark red prisms, m. p. 164°.

p-2-*Nitrobenzylideneaminodimethylaniline*,

$$NO_2\cdot C_6H_4\cdot CH⁚N\cdot C_6H_4\cdot NMe_2,$$

separates from light petroleum in dark red crystals, m. p. 90°.

When *o*-nitrobenzaldehyde dissolved in toluene and *p*-aminophenol hydrochloride and aqueous sodium acetate are brought together, condensation does not occur, but the *additive* compound,

$$NO_2\cdot C_6H_4\cdot CH(OH)\cdot NH\cdot C_6H_4\cdot OH,$$

is formed; it crystallises from toluene in yellow needles, m. p. 156°. *o*-Aminophenol, under similar conditions, also gives a corresponding additive *compound*, which crystallises from carbon tetrachloride in yellow needles, m. p. 104°.

By slightly modifying the conditions, however, 4-o-*nitrobenzylideneamino-α-naphthol*, $NO_2\cdot C_6H_4\cdot CH⁚N\cdot C_{10}H_6\cdot OH$, can be obtained; it crystallises from chloroform or light petroleum in yellow needles, m. p. 148°. 1-o-*Nitrobenzylideneamino-β-naphthol* crystallises from carbon tetrachloride or toluene in yellow needles, m. p. 123°. p-2-*Nitrocinnamylideneaminodimethylaniline* separates from alcohol in dark red needles, m. p. 90°. p-2-*Nitrocinnamylideneaminophenol* separates from toluene in yellow crystals, m. p. 168°; the corresponding *o*-aminophenol *derivative* crystallises from alcohol in well-formed, golden prisms, m. p. 125°. 4-o-*Nitrocinnamylideneamino-α-naphthol* crystallises from a mixture of acetone and light petroleum in brownish-yellow plates, m. p. 173°; the corresponding *derivative* of 1-amino-β-naphthol crystallises from chloroform containing light petroleum in yellowish-brown needles, m. p. 100°. o-*Nitrocinnamylideneaminosalicylic acid*,

$$[\mathrm{CH{:}N : OH : CO_2H = 5 : 2 : 1}],$$

forms yellow crystals, m. p. 194°.

p-3-*Nitrobenzylideneaminodimethylaniline* crystallises from carbon tetrachloride or ether in orange-yellow plates, m. p. 156°. *m*-Nitrobenzaldehyde combines with *p*-aminophenol to form the *additive* compound, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}NH{\cdot}C_6H_4{\cdot}OH}$, which crystallises from toluene in large, dark yellow plates, m. p. 158°; the analogous compound from *o*-aminophenol crystallises from carbon tetrachloride in slightly yellow needles, m. p. 131°. 4-m-*Nitrobenzylideneamino-α-naphthol* crystallises from a mixture of xylene and toluene in brownish-yellow plates, m. p. 184°; the corresponding 1-amino-β-naphthol *derivative* crystallises in yellow needles, m. p. 105°.

p-3-*Nitrocinnamylideneaminodimethylaniline* crystallises from ethyl acetate and light petroleum in bright red leaflets, m. p. 192°. p-3-*Nitrocinnamylideneaminophenol* crystallises from alcohol in rhombic, yellow plates, m. p. 196°; the corresponding *o*-aminophenol *derivative* crystallises from carbon tetrachloride in slender, yellow needles, m. p. 137°. 4-m-*Nitrocinnamylideneamino-α-naphthol* crystallises from alcohol containing xylene in yellow, rhombic plates, m. p. 204°; the analogous *derivative* from 1-amino-β-naphthol crystallises from carbon tetrachloride in dark yellow needles, m. p. 164°. m-*Nitrocinnamylideneaminosalicylic acid* $[\mathrm{CH{:}N : OH : CO_2H = 5 : 2 : 1}]$ crystallises in bright red, lanceolate needles, m. p. 198°.

p-Nitrobenzaldehyde combines with *p*-aminophenol to form the *additive* compound, $\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}NH{\cdot}C_6H_4{\cdot}OH}$, which crystallises from ether or toluene in intensely yellow prisms, m. p. 166°; the analogous *derivative* from *o*-aminophenol crystallises from carbon tetrachloride in yellow needles, m. p. 158°. p-4-*Nitrocinnamylideneaminodimethylaniline* crystallises from toluene in red, hexagonal plates, m. p. 227°. p-4-*Nitrocinnamylideneaminophenol* crystallises from alcohol in yellow needles, m. p. 191°; the analogous *o*-aminophenol *derivative* is similar, m. p. 158°. 4-p-*Nitrocinnamylideneamino-α-naphthol* crystallises from ethyl acetate or chloroform in red needles, m. p. 210°; the corresponding *derivative* of 1 : 2-aminophenol crystallises from alcohol containing acetone in bright red plates, m. p. 164°. p-*Nitrocinnamylideneaminosalicylic acid* $[\mathrm{CH{:}N : OH : CO_2H = 5 : 2 : 1}]$ crystallises from alcohol in stellate aggregates of reddish-yellow needles, m. p. 155°.

p-4-*Dimethylaminobenzylidene*-p-*aminophenol*,

$$\mathrm{NMe_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}OH},$$

prepared from *p*-dimethylaminobenzaldehyde and *p*-aminophenol, crystallises from alcohol containing dilute acetic acid in yellow prisms, m. p. 265°; the corresponding *derivative* of *o*-aminophenol crystallises from alcohol or light petroleum in yellow needles, m. p. 119°. 4-p-*Dimethylaminobenzylideneamino-α-naphthol* crystallises from xylene in yellow needles, m. p. 199°; the corresponding *derivative* from 1-amino-β-naphthol crystallises from toluene in yellow leaflets, m. p. 109°. p-*Dimethylaminobenzylideneaminosalicylic acid* $[\mathrm{CH{:}N : OH : CO_2H = 5 : 2 : 1}]$ forms bright red crystals, m. p. 265°, and is sparingly soluble in all solvents. p-4-*Dimethylaminocinnamylideneaminodimethylaniline* crystallises from light petroleum and ethyl acetate in brownish-yellow needles, m. p. 196°. p-4-*Dimethylaminocinnamylideneaminophenol* forms brownish-yellow crystals, m. p. 260°; the corresponding derivative from *o*-aminophenol crystallises from carbon tetrachloride in brown plates, m. p. 143°. p-*Dimethylaminocinnamylideneaminocinnamic acid* forms dark red needles, m. p. 206°.

The colour and structure of the compounds described are compared by means of a table, and the following conclusions drawn. The group C:C exercises a marked influence on the colour of the azomethine compounds. A nitro-group introduced into the nucleus of the aldehyde portion darkens the colour; the influence exerted is greatest when the group is in the para-position, somewhat less when in the ortho-, and least in the meta-position; analogous observations have been made in the case of the fulgides (Stobbe, Abstr., 1906, i, 91, 183, 278). The auxochromic dimethylamino-group, NMe_2, exercises less influence in darkening the colour than the chromophore NO_2 in the same position in the aldehydic component. The auxochromes OH and NMe_2 also darken the colour when present as substituents in the aminic component, the influence of the NMe_2 being the greater. The influence of hydroxyl is greatest when it is present in the ortho-position.

W. A. D.

5-Nitroguaiacol. FRÉDÉRIC REVERDIN and PIERRE CRÉPIEUX (*Ber.*, 1906, **39**, 4232).—The compound described by the authors as 4-nitroguaiacol (Abstr., 1903, i, 624) is really the 5-nitro-isomeride (compare Paul, Abstr., 1906, i, 843). C. S.

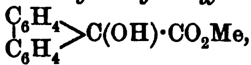
Sulphonation of Guaiacol. ADOLF RISING (*Ber.*, 1906, **39**, 3685—3693).—A mixture of almost equal amounts of α- and β-guaiacolsulphonic acids is primarily obtained by the sulphonation of guaiacol independently of the temperature conditions. The potassium salt of the α-acid is identical with the "free *o*-guaiacolsulphonic acid" described by Barell (*Pharm. Zeit.*, 1899, No. 13) and with the potassium salt of *p*-guaiacolsulphonic acid described by von Heyden (*Patentanmeldung*, C 18820, Kl. 12g.) and with the para-salt described by Paul (Abstr., 1906, i, 843). The basic calcium salt of the β-acid corresponds with von Heyden's basic calcium salt of "*o*-guaiacolsulphonic acid." When heated above 100°, both the α- and β-acids are transformed into a third acid, the γ-acid. The potassium salt of the γ-acid is identical with the "free *p*-guaiacolsulphonic acid" of Barell and with the compound described by F. Hoffman-La Roche & Co. (D.R.-P., 105052). The pharmaceutical preparations "Thiocol" and "Kalium sulfoguajacolicum" are mixtures of normal and basic potassium salts of α- and β-guaiacolsulphonic acids. In the α-acid the groups OH, OMe, SO_3H are in the positions 1, 2, and 4 respectively, in the β-acid in the positions 1, 2, and 5, and in the γ-acid in the vicinal position.

The γ-acid forms colourless crystals, m. p. 92°. A. McK.

3- or 6-Guaiacolsulphonic Acid. LUDWIG PAUL (*Ber.*, 1906, **39**, 4093—4095).—Barell's *p*-guaiacolsulphonic acid (*Pharm. Zeit.*, 1899, No. 13) and Rising's *v*-guaiacolsulphonic acid (preceding abstract) are both catechol-4-sulphonic acid which is converted by potassium hydroxide and methyl iodide into potassium veratrolesulphonate (Abstr., 1906, i, 843). Hence the isomeric change of 4- or 5- into *v*-guaiacolsulphonic acid assumed by Rising (*loc. cit.*) does not take place. G. Y.

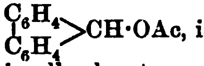
Propylguaiacol. PARRAIN (*Bull. Soc. chim.*, 1906, [iii], **35**, 1098—1099).—*Propylguaiacol*, $OMe\cdot C_6H_3Pr^{\alpha}\cdot OH$ (3 : 1 : 4), was isolated from the mixed phenols present in wood creosote by agitating the former with milk of strontia and fractionally distilling the phenols regenerated from the mixed insoluble strontium derivatives thus formed. It is purified finally through the benzoyl derivative, and then is a colourless liquid with an odour of cloves, b. p. 246°, D^0 1·060, D^{15} 1·049, and on treatment with hydrogen bromide at 100° yields 3 : 4-dihydroxy-1-propylbenzene. The *benzoyl* derivative, m. p. 72°, crystallises from alcohol, and the *carbonate* crystallises in needles, m. p. 66°. T. A. H.

9-Dihydroxyfluorene and Stereoisomeric 9-Acetoxyfluorenes. JULIUS SCHMIDT and ROBERT MEZGER (*Ber.*, 1906, **39**, 3895—3901. Compare Abstr., 1906, i, 27).—*Methyl* 9-*hydroxyfluorene*-9-*carboxylate* (*methyl diphenyleneglycollate*),



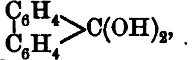
$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C(OH)\cdot CO_2Me$

obtained by the catalytic method of esterification, crystallises from 60 per cent. ethyl alcohol in rhombic prisms, m. p. 158—160°. The *ethyl* ester and its *acetyl* derivative melt at 96° and 103—104° respectively; the *acetyl* derivative of the methyl ester crystallises in colourless plates, m. p. 147—148°. When 9-acetoxyfluorene-9-carboxylic acid is boiled for five hours with acetic anhydride, carbon dioxide is eliminated and a mixture of two stereoisomeric 9-*acetoxyfluorenes* (*fluorenyl acetates*),



$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>CH\cdot OAc$

is formed. The β-compound is less readily soluble in all solvents, crystallises from glacial acetic acid in minute, colourless prisms, m. p. 208—209°. When heated with ethyl alcohol at 200°, it is transformed into the isomeric α-compound, which crystallises from alcohol in long, colourless prisms, m. p. 169—170°. Both compounds dissolve in concentrated sulphuric acid, yielding blue solutions. When hydrolysed by boiling with concentrated hydrochloric acid in a reflux apparatus, the α-acetyl derivative yields 9-*dihydroxyfluorene*,



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C(OH)_2,$$

in the form of colourless, glistening plates, m. p. 94°. Its constitution follows from the readiness with which it loses water, yielding fluorenone. J. J. S.

Alkylation of the Nucleus of Phenols. JOSEF HERZIG and FRANZ WENZEL (*Monatsh.*, 1906, **27**, 781—802. Compare Abstr., 1904, i, 246; Herzig and Zeisel, Abstr., 1888, 822; 1889, 247, 966). —In view of Kaufler's rule (Abstr., 1901, i, 206) that on the alkylation of tautomeric substances the tendency to the formation of the true ether increases with the size of the alkyl group, the amount of the ψ-ester formed being correspondingly decreased, the meagre results obtained in the nucleus alkylation of phenols may be ascribed to the employment of ethyl iodide, and further progress was to be expected from the study of the methyl derivatives.

The action of diazomethane on phloroglucinol in ethereal solution leads to the formation of the trimethyl ether in a 37% yield, together with a mixture of the mono- and di-methyl ethers, that of methyl sulphate on phloroglucinol in alkaline solution to the formation of the trimethyl ether in a 37·9% yield, together with a mixture of the mono- and di-methyl ethers. The trimethyl ether is formed also in a 65% yield when phloroglucinol is heated with methyl iodide and sodium methoxide in methyl-alcoholic solution on the water-bath. In both experiments in alkaline solution, small amounts of an oil which is insoluble in alkali hydroxides and is the product of the nucleus alkylation are obtained.

[With E. HORNSTEIN.]—The action of methyl iodide on orcinol or orcinolcarboxylic acid in presence of a large excess of an alkali hydroxide leads to the formation of tetramethyl-ψ-orcinol (4 : 6-diketo-2 : 3 : 3 : 5 : 5-pentamethyl-Δ′-*cyclo*hexene ?), $C_{11}H_{16}O_2$, (Abstr., 1904, i, 246), which crystallises from alcohol in long, glistening needles, m. p. 63°, b. p. about 128°/17 mm., and forms a crystalline *bromide*.

If the product obtained by heating orcinolcarboxylic acid with methyl iodide in alkaline methyl-alcoholic solution is treated with an alkali hydroxide and the insoluble portion distilled, the fraction with the highest boiling point contains a *substance*, $C_9H_7O(OMe)_3$, m. p. 84°; on hydrolysis with boiling potassium hydroxide, this yields the *dimethyl ether* of methylorcinolcarboxylic acid, $C_6HMe_2(OMe)_2{\cdot}CO_2H$, which crystallises in quadratic leaflets, m. p. with decomposition 183°. The portion of the original product soluble in alkali hydroxides contains β-orcinol; this does not react with diazomethane. The *diacetate* of β-orcinol, $C_6H_2Me_2(OAc)_2$, crystallises from alcohol in long, white needles, m. p. 69°.

Kurzweil's dimethylorcinol (*Monatsh.*, 1903, **24**, 747) could not be isolated from the products of the action of methyl iodide on orcinolcarboxylic acid.

The methylation of orcinolcarboxylic acid by means of methyl iodide in ethyl-alcoholic solution leads to the formation of tetramethyl-ψ-orcinol, the trimethyl ether-ester, m. p. 84°, and *methylorcinol* (3 : 5-*dihydroxy*-1 : 2-*dimethylbenzene*), $C_6H_2Me_2(OH)_2$, which is isomeric with β-orcinol. It crystallises from benzene in glistening, silky needles, m. p. 115—117°, b. p. 170—180°/12 mm., and is soluble in aqueous alkali hydroxides; with diazomethane in ethereal solution it forms a *monomethyl ether*, $OH{\cdot}C_6H_2Me_2{\cdot}OMe$, which crystallises from benzene; m. p. 83°, b. p. 192—202°/20 mm. With bromine in glacial acetic acid solution, methylorcinol forms a *monobromo*-derivative,

$$C_6HBrMe_2(OH)_2,$$

which crystallises from 50% acetic acid, m. p. 142°.

The experiments in the nucleus methylation of orcinol are carried out under the same conditions as those with the carboxylic acid, but only in ethyl-alcoholic solution. The portion of the product soluble in alkali hydroxides deposits directly a *substance*, $(C_8H_4O)_n$, which crystallises from alcohol; m. p. 187—192°, decomposing. On distillation the remainder of this portion of the product yields *dimethylorcinol*, $C_9H_{12}O_2$, which crystallises from benzene in long, white needles, m. p. 145—147°, together with the *methyl ether* of β-orcinol (2-*hydroxy*-6-*methoxy*-1:4-*xylene*), $OH{\cdot}C_6H_2Me_2{\cdot}OMe$, m. p. 118—121°; this crystallises from benzene, and on hydrolysis yields β-orcinol.

The portion of the original product insoluble in alkali hydroxides yields tetramethyl-ψ-orcinol and the methyl ether of β-orcinol.

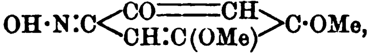
G. Y.

Action of Nitric Acid and of Nitrous Acid on Asaronic Acid. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1906, **39**, 3679—3685).—When asaronic acid is nitrated in glacial acetic acid solution with concentrated nitric acid, it forms 4-*nitro*-1:2:5-*trimethoxybenzene*, $C_6H_2(OMe)_3{\cdot}NO_2$, m. p. 130°, and forms a red solution with concentrated sulphuric acid.

4-*Amino*-1:2:5-*trimethoxybenzene* (*asarylamine*), $C_6H_2(OMe)_3{\cdot}NH_2$, obtained by the reduction of the preceding compound with tin and hydrochloric acid, separates from a mixture of benzene and light petroleum in felted, slightly pink needles, m. p. 95°, unstable in moist air. Its *benzoyl* derivative crystallises from alcohol in needles, m. p. 138°.

4 (1 : 2 : 5)-*Trimethoxybenzylidene*-4-*amino*-1 : 2 : 5-*trimethoxybenzene* (*asarylasarylideneamine*), $C_6H_2(OMe)_3{\cdot}CH{:}N{\cdot}C_6H_2(OMe)_3$, obtained by the addition of a few drops of concentrated hydrochloric acid to a solution of a mixture of asarylaldehyde and asarylamine in ethyl alcohol, separates from alcohol in greenish-yellow needles, m. p. 142·5°.

4 : 5-*Dimethoxy*-o-*benzoquinoneoxime*,



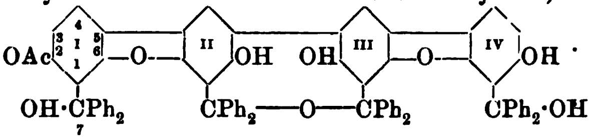
$$\mathrm{OH{\cdot}N{:}C}<\begin{matrix}\mathrm{CO{=\!=\!=}CH}\\ \mathrm{CH{:}C(OMe)}\end{matrix}>\mathrm{C{\cdot}OMe},$$

which may be the tautomeric 4-*nitroso*-1:2-*dimethoxy*-5-*phenol*, is obtained by boiling an aqueous solution of asaronic acid with an excess of sodium nitrite; it forms glistening, ruby-red crystals. When heated, it decomposes explosively. It does not give the Liebermann reaction for nitroso-phenols. Its *acetyl* derivative forms yellow crystals, m. p. 195—197°, decomposing. Its *benzoyl* derivative forms yellow needles, m. p. 190—193°, decomposing. When reduced by tin and hydrochloric acid, it forms 6-*amino*-3 : 4-*dimethoxyphenol*,

$$NH_2{\cdot}C_6H_2(OMe)_2{\cdot}OH,$$

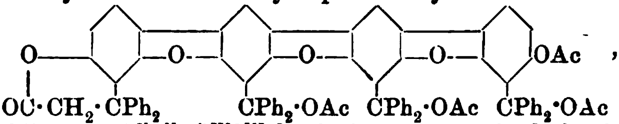
m. p. 152°, and yields on benzoylation, 6-*benzoylamino*-3 : 4-*dimethoxyphenyl benzoate*, $NHBz{\cdot}C_6H_2(OMe)_2{\cdot}OBz$, which separates from glacial acetic acid in leaflets, m. p. 209°, decomposing. A. McK.

Condensation of Benzil with Resorcinol. II. Derivatives of m-Tetra-2:6-dihydroxytritanol. HANS VON LIEBIG [and, in part, H. HÖRT] (*J. pr. Chem.*, 1906, [ii], **74**, 345—419. Compare Abstr., 1905, i, 781).—The condensation of benzil with resorcinol by fusion with potassium hydroxide or carbonate at 130—140° leads to the formation of ten substances. When boiled with glacial acetic acid, the mixture of products yields a red dye, 2^{I}-acetoxy-$\overline{m}$-tetra-2 : 6-dihydroxytritanol-$6^{\mathrm{I}}2^{\mathrm{II}}$: $6^{\mathrm{III}}2^{\mathrm{IV}}$-diether-$7^{\mathrm{II}}7^{\mathrm{III}}$-anhydride,

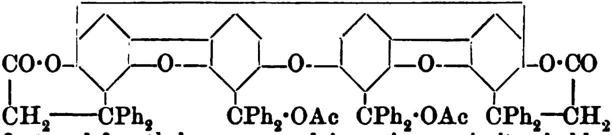


(The word "tritan" represents the triphenylmethane nucleus, $Ph_3C\cdot$, "ether" denotes the phenyl ether linking Ph·O·Ph, and $\bar{o}$, $\overline{m}$, $\bar{p}$ before the Greek numerals, tetra, &c., indicate that a direct union takes place between the corresponding number of phenyl groups (in the above case, four) in the *o*-, *m*-, or *p*-position. "Anhydride" indicates the etheric union between the aliphatic carbon atoms, and "anhydro" denotes that water has been eliminated between the groups numbered.)

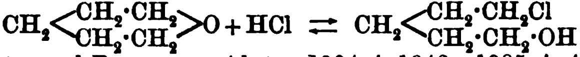
The constitution and spacial relations of this and its derivatives are discussed. Those in which the second and third benzene nuclei are in close proximity as the $2^{\mathrm{I}}7^{\mathrm{I}}$-anhydropenta-acetyl derivative of the triether,



, are yellow, whilst the $7^{\mathrm{II}}6^{\mathrm{II}}$: $7^{\mathrm{III}}2^{\mathrm{III}}$-dianhydrotetra-acetyl derivative of the triether,



, in which the first and fourth benzene nuclei are in proximity, is blue; the red dye occupies an intermediate position in the series. With the exception of the blue dianhydrotetra-acetyl-triether, all the coloured substances of this group are quinones, or contain an ether or an anhydride linking between the second and third benzene nuclei, whilst in the colourless substances these are joined only by a C–C linking. All the coloured substances cannot be formulated as quinones, and it is suggested that the cause of colour in organic compounds may be the relative arrangement in space of a number of ethylene linkings.

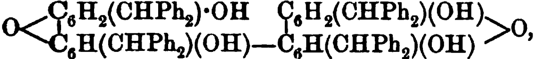
Some of the derivatives of $\overline{m}$-tetra-2 : 6-dihydroxytritanol form *additive* compounds with hydrogen chloride which are not decomposed by water, and according to Collie and Tickle's theory (Trans., 1899, **75**, 710) must be salts of oxonium bases. A number of objections to the oxonium theory are raised, and it is urged that the formation of the so-called oxonium salts is explained better by assuming an opening of the ring and the formation of a chlorohydrin or other derivative of a glycol,  $CH_2{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}O + HCl \rightleftarrows CH_2{<}^{CH_2\cdot CH_2Cl}_{CH_2\cdot CH_2\cdot OH}$ (compare Willstätter and Pummerer, Abstr., 1904, i, 1043; 1905, i, 457; Diels and Rosenmund, Abstr., 1906, i, 673).

2^{I}-*Acetoxy*-m̄-*tetra*-2 : 6-*dihydroxytritanol*-$6^{I}2^{II}$: $6^{III}2^{IV}$-*diether*-$7^{II}7^{III}$-*anhydride*, $C_{78}H_{54}O_{10}$, crystallises from alcohol, acetone, or glacial acetic acid in slender, yellow needles or rectangular leaflets from alcohol and aqueous ammonia on evaporation of the ammonia in brown, rectangular rods, m. p. 288°; it forms yellow solutions having a lively green fluorescence, gives with concentrated sulphuric acid a violet, with acetic anhydride and concentrated sulphuric acid a deep violet coloration, becoming red on addition of alcohol. When distilled alone or with zinc dust, it decomposes very readily in the form of its alkali salts, forming diphenylmethane; only benzaldehyde, benzoic acid, and resorcinol can be isolated from the product obtained on fusion with potassium hydroxide or on oxidation. The *sodium*,

$$C_{78}H_{51}O_{10}Na_3,C_2H_6O,$$

and *potassium*, $C_{78}H_{51}O_{10}K_3,C_2H_6O$, salts are described.

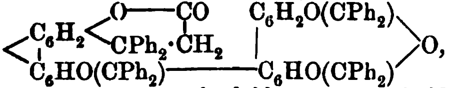
When boiled with zinc dust and glacial acetic acid, the acetoxy-anhydride is reduced to m̄-*tetra*-2 : 6-*dihydroxytritan*-$6^{I}2^{II}$: $6^{III}2^{IV}$-*diether*,



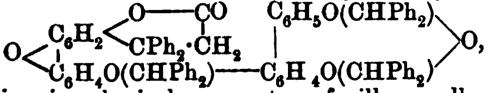
$$O\Big\langle\begin{matrix}C_6H_2(CHPh_2)\cdot OH & C_6H_2(CHPh_2)(OH)\\ | & | \\ C_6H(CHPh_2)(OH) - & C_6H(CHPh_2)(OH)\end{matrix}\Big\rangle O$$

, which crystallises from benzene in colourless prisms containing C_6H_6, loses C_6H_6 at 150°, m. p. 215—216°, and forms colourless solutions with blue fluorescence.

$2^{I}7^{I}$-*Anhydro*-2^{I}-*acetoxy*-m̄-*tetra*-2 : 6-*dihydroxytritan*-I-*ol*-II, III, IV-*one*-$6^{I}2^{II}$,$6^{III}2^{IV}$-*diether* (brown *tritanone* ether),

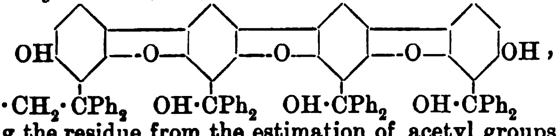


formed by heating the acetoxy-anhydride at 280—320°, crystallises from benzene in glistening, dark brown leaflets, m. p. 273°, dissolves in chloroform, forming a brown solution with green fluorescence, forms brownish-violet *salts* with mineral acids, and when boiled with acetic anhydride and sodium acetate is converted into the red tritanone ether and its acetyl derivatives. When reduced with zinc dust and glacial acetic acid, the brown tritanone ether yields a *product*,



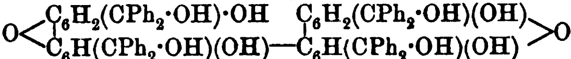
which crystallises in spherical aggregates of silky needles, m. p. with decomposition 213—215°.

m̄-*Tetra*-2 : 6-*dihydroxytritan*-II, III, IV-*ol*-I-*acetic acid*-$6^{I}2^{II}$: $6^{II}2^{III}$: $6^{III}2^{IV}$-*triether*,



is obtained by boiling the residue from the estimation of acetyl groups in the anhydropenta-acetyl derivative of the triether successively with dilute ammonia, acetic acid, and benzene, and crystallising the insoluble remainder from much alcohol; it crystallises in yellow leaflets, m. p. above 300°. On evaporation of the benzene solution, there is obtained a varnish and a few colourless crystals, m. p. 167—168°.

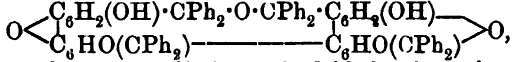
When boiled with potassium hydroxide and alcohol, the acetoxy-diether-anhydride is converted into (*a*) m̄-*tetra*-2 : 6-*dihydroxytritanol*-$6^{I}2^{II} : 6^{II}2^{III} : 6^{III}2^{IV}$-*triether*, $C_{76}H_{52}O_9$, which crystallises from alcohol or acetone in yellow leaflets, does not melt at 300°, and forms yellow solutions with brilliant green fluorescence, and (*b*) m̄-*tetra*-2 : 6-*dihydroxytritanol*-$6^{I}2^{II} : 6^{III}2^{IV}$-*diether*,



$$O<\begin{array}{l} C_6H_2(CPh_2\cdot OH)\cdot OH \quad C_6H_2(CPh_2\cdot OH)(OH) \\ C_6H(CPh_2\cdot OH)(OH) - C_6H(CPh_2\cdot OH)(OH) \end{array}>O,$$

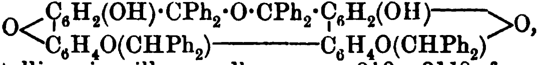
which forms a brown, crystalline mass, m.p. 151°.

m̄-*Tetra*-2 : 6-*dihydroxytritan*-I, IV-*one*-II, III-*ol*-$6^{I}2^{II} : 6^{III}2^{IV}$-*diether*-$7^{II}7^{III}$-*anhydride* (*red tritanone ether*),



$$O<\begin{array}{l} C_6H_2(OH)\cdot CPh_2\cdot O\cdot CPh_2\cdot C_6H_2(OH) - \\ C_6HO(CPh_2) \text{———————} C_6HO(CPh_2) \end{array}>O,$$

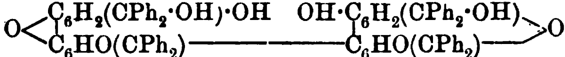
is formed from the acetoxy-diether-anhydride by the action of hydrogen chloride in boiling alcoholic solution, by boiling with glacial acetic acid and a small amount of concentrated sulphuric acid, by heating with concentrated hydrochloric acid at 100—200° under pressure, or by shaking with acetic anhydride and sulphuric acid, and from the diacetyl derivative of the diether by the action of heat. It crystallises from benzene in glistening, scarlet, hexagonal leaflets, from chloroform in slender, red needles, m. p. 274°, has a green fluorescence in chloroform solution, dissolves in alcoholic potassium hydroxide forming a red solution with green fluorescence, becoming colourless, and depositing a red substance on addition of water, and forms crystalline, violet *salts* with mineral acids. On reduction it yields a *product*,



$$O<\begin{array}{l} C_6H_2(OH)\cdot CPh_2\cdot O\cdot CPh_2\cdot C_6H_2(OH) \text{——} \\ C_6H_4O(CHPh_2) \text{————} C_6H_4O(CHPh_2) \end{array}>O,$$

which crystallises in silky needles, m. p. 210—211°, forms solutions with blue fluorescence, and is converted again into the red ether.

When heated successively with ammonia and acetic acid and re-crystallised from alcohol, the red residue obtained on estimation of the acetyl groups in the *a*-diacetyl derivative of the diether anhydride yields m̄-*tetra*-2 : 6-*dihydroxytritan*-I, IV-*one*-II, III-*ol*-$6^{I}2^{II} : 6^{III}2^{IV}$-*diether*,



$$O<\begin{array}{l} C_6H_2(CPh_2\cdot OH)\cdot OH \quad OH\cdot C_6H_2(CPh_2\cdot OH) \\ C_6HO(CPh_2) \text{——————} C_6HO(CPh_2) \text{——} \end{array}>O,$$

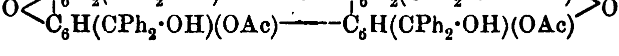
which forms a red powder, commences to sinter at 160°, m. p. 200°, swells up above 200°, dissolves in alcohol, forming a dark red solution decolorised on addition of aqueous potassium hydroxide, and gives a violet coloration with concentrated sulphuric or hydrochloric acid.

When heated with concentrated sulphuric acid on the water-bath, the acetoxy-diether-anhydride yields a *tetrasulphonic* acid,

$$C_{78}H_{50}O_{10}(SO_3H)_4,$$

which crystallises in dark red leaflets, m. p. above 330°, is soluble in cold water or alcohol, forming red solutions becoming dark red with slight green fluorescence on addition of potassium hydroxide, and gives a dark coloration with ferric chloride.

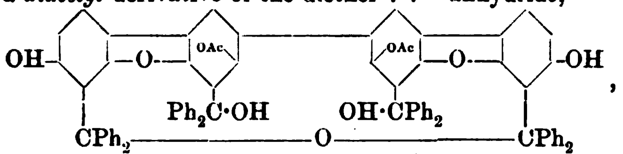
$2^{II}2^{III}$-*Diacetoxy*-m̄-*tetra*-2 : 6-*dihydroxytritanol*-$6^{I}2^{II} : 6^{III}2^{IV}$-*diether*,



$$O<\begin{array}{l} C_6H_2(CPh_2\cdot OH)\cdot OH \quad OH\cdot C_6H_2(CPh_2\cdot OH \text{——}) \\ C_6H(CPh_2\cdot OH)(OAc) \text{——} C_6H(CPh_2\cdot OH)(OAc) \end{array}>O,$$

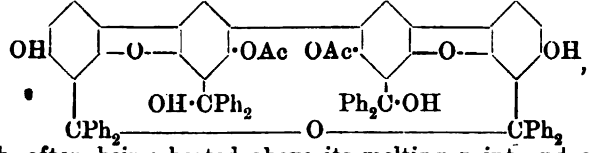
prepared together with the tetra-acetyl derivative by heating the acetoxy-diether-anhydride with acetic anhydride and concentrated sulphuric acid on the water-bath, and crystallising the product from a mixture of ether and light petroleum, crystallises from ether on evaporation in glistening leaflets. On evaporation of the ether-light petroleum filtrate and treatment of the residue with cold benzene, there are obtained the tetra-acetyl derivative and an *additive* compound of the diacetyl-diether and benzene, $C_{80}H_{58}O_{12},C_6H_6$, which is formed also by the action of cold benzene on the diacetyl-diether or the α-diacetyl-diether-anhydride; it crystallises in slender, white needles, sinters at 130°, swells up at 140—143°, and resolidifies and melts again at 205—206°; when boiled with benzene it is converted into the benzene additive compound of β-diacetyl-diether-anhydride. The *additive* compound, $C_{80}H_{58}O_{12},C_4H_8O_2$, formed by evaporating the solution of the diacetyl-diether or α-diacetyl-diether-anhydride in ethyl acetate, crystallises in long, rectangular leaflets, and decomposes at 140°, losing ethyl acetate and water, and after resolidifying has m. p. 205—206°.

The *α-diacetyl* derivative of the diether-$7^{I}7^{IV}$-anhydride,



, formed by boiling the diacetyl-diether with ether, crystallises in rhombic leaflets, m. p. 150°, and again at 205—206°, and is converted by boiling acetone and benzene into the corresponding additive compounds of the β-derivative.

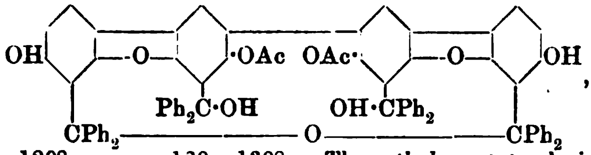
The *additive* compound of the β-diacetyl derivative and benzene, $C_{80}H_{56}O_{11},3C_6H_6$, crystallises in slender, white needles or long, rectangular plates, loses $2C_6H_6$ slowly at the laboratory temperature but quickly on the water-bath, sinters at 150°, m. p. 208—209°, and is converted by boiling acetone into the corresponding acetone compound, or by boiling alcohol partially into the additive compound of the γ-diacetyl derivative. The *additive* compound of acetone and the β-diacetyl-diether-anhydride, $C_{80}H_{56}O_{11},C_3H_6O$, crystallises in glistening rhombohedra, loses C_3H_6O on the water-bath, m. p. 208°, and on prolonged heating on the water-bath yields the *β-diacetyl-diether-anhydride*,



, m. p. 208°, which, after being heated above its melting point and cooled, resolidifies and then has m. p. 120—130°.

The *ethyl alcohol* derivative of the γ-diacetyl-diether-anhydride, $C_{80}H_{54}O_{10},C_2H_6O$, formed by shaking the diacetyl-diether with alcohol and evaporating the solution, or by boiling any of the diacetyl derivatives with ethyl alcohol, crystallises in slender needles or pointed, rhombic leaflets, sinters at 180°, m. p. 180—182°, and when heated at 190—200° for some minutes yields the *γ-diacetyl-diether-*

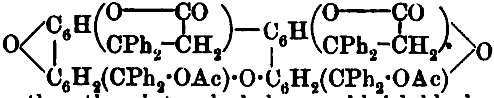
anhydride,



, which sinters at 120°, m. p. 120—130°. The *ethyl acetate* derivative, $C_{80}H_{54}O_{16},C_4H_8O_2$, formed by the action of boiling ethyl acetate on the γ-diacetyl compound or its alcohol or acetone derivative, separates in glistening, microscopic, double pyramids, and loses $C_4H_8O_2$ at 190°, m. p. 190—191°. The *acetone* derivative, $C_{80}H_{56}O_{11},C_3H_6O$, crystallises in white, pointed, rhombic needles or leaflets, m. p. 180—190°. The *methyl alcohol* derivative, $C_{80}H_{54}O_{10},CH_4O$, formed by boiling the compounds of the α- and β-diacetyl series with methyl alcohol, crystallises in hexagonal leaflets, m. p. 210°.

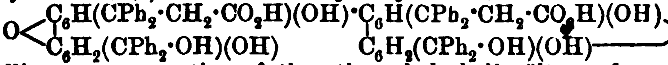
These diacetyl compounds decompose on prolonged heating, forming the red tritanone ether; they form solutions having a slight blue fluorescence, and dissolve in a small amount of glacial acetic acid to a violet, in much acetic acid to a green solution which gradually becomes red. Violet *oxonium* salts are formed on addition of concentrated hydrochloric or sulphuric acid to the solid compounds or to the solutions in glacial acetic acid or alcohol; the diacetyl compounds behave towards alkali hydroxides in the same manner as the red tritanone ether, and are hydrolysed by alcoholic potassium hydroxide. The constitutions of the diacetyl-compounds and of their additive compounds are discussed.

If one of the diacetyl compounds or the brown or red tritanone ether is boiled with sodium acetate and acetic anhydride and poured into water, a greyish-black precipitate is formed, which on extraction with ether yields a residue of the red tritanone ether. The ethereal solution contains three products: (*a*) $7^{II}6^{II}:7^{III}2^{III}$-*dianhydro-tetra-acetyl*-$\overline{\text{m}}$-*tetra*-2 : 6-*tritanol*-II, I; I, IV; IV, III-*triether* (*blue tetra-acetyl* derivative),



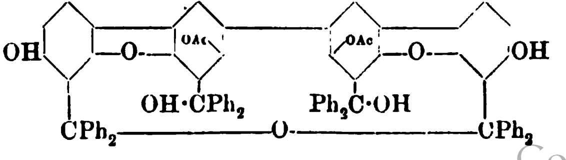
$$O\left<\begin{array}{l}C_6H\left(\begin{array}{l}O\text{——}CO\\CPh_2-CH_2\end{array}\right)-C_6H\left(\begin{array}{l}O\text{——}CO\\CPh_2-CH_2\end{array}\right)\\C_6H_2(CPh_2\cdot OAc)\cdot O\cdot C_6H_2(CPh_2\cdot OAc)\end{array}\right>O$$

, crystallises on pouring the ether into alcohol as a bluish-black powder, m. p. about 200°, forms blue solutions, is precipitated from its alcoholic solution by hydrochloric acid as a blue, by sulphuric acid as a brown powder, gives a characteristic milky-blue coloration with alcoholic ammonia, and yields an olive-green solution when boiled with alcoholic potassium hydroxide; (*b*) $\overline{\text{m}}$-*tetra*-2 : 6-*dihydroxytritan*-I, IV-*ol*-II, III-*acetic acid*,



$$O\left<\begin{array}{ll}C_6H(CPh_2\cdot CH_2\cdot CO_2H)(OH)\cdot & C_6H(CPh_2\cdot CH_2\cdot CO_2H)(OH)\\C_6H_2(CPh_2\cdot OH)(OH) & C_6H_2(CPh_2\cdot OH)(OH)\end{array}\right>O$$

, crystallises on evaporation of the ethereal-alcoholic filtrate from (*a*), is washed with ether, and recrystallised from a mixture of acetone and alcohol; it forms slender, white needles, m. p. 222—224°; (*c*) the δ-*diacetyl-diether-anhydride*,



,

crystallises from the ethereal washings of the preceding substance on evaporation with alcohol in red needles, m. p. with decomposition 180—190°, and on prolonged boiling with alcohol forms $7^{\mathrm{II}}6^{\mathrm{II}}$: $7^{\mathrm{III}}2^{\mathrm{III}}$-*dianhydro*-m̄-*tetra*-2 : 6-*dihydroxytritan*-I,IV-*ol*-II,III-*acetic acid*-$7^{\mathrm{I}}7^{\mathrm{IV}}$-*anhydride*, $C_{80}H_{52}O_{9},2C_2H_6O$, m. p. 180—190°. These three acetyl compounds lose acetic acid when strongly heated but do not form a tritanone ether.

The *tetra-acetyl* derivative of the diether, $C_{84}H_{62}O_{14}$, formed together with the diacetyl derivative, is obtained on evaporation of its benzene solution as a varnish or on addition of its benzene or ethereal solution to light petroleum as a yellow, amorphous precipitate, sinters at 115°, and on further heating melts slowly, becomes viscid, and melts again at 190°; when heated above 200° it loses acetic anhydride and forms the brown tritanone ether. $2^{\mathrm{I}}7^{\mathrm{I}}$-*Anhydrotetra-acetyl*-m̄-*tetra*-2 : 6-*dihydroxytritanol*-$6^{\mathrm{I}}2^{\mathrm{II}}$: $6^{\mathrm{III}}2^{\mathrm{IV}}$-*diether*, $C_{84}H_{60}O_{13}$, crystallises when the ethereal solution of the preceding substance is poured into alcohol as a yellowish-white, sandy powder, when heated behaves in the same manner as the tetra-acetyl derivative, and forms brownish-violet oxonium salts of the brown tritanone ether when treated with concentrated hydrochloric or sulphuric acid.

When boiled with sodium acetate and acetic anhydride, the acetoxy-diether-anhydride yields three products: (*a*) the $2^{\mathrm{I}}7^{\mathrm{I}}$-*anhydropenta-acetyl* derivative of the triether, $C_{86}H_{60}O_{18}$, crystallises from a mixture of alcohol and chloroform in yellow or reddish-yellow, quadratic leaflets, m. p. 247°, loses acetic acid when strongly heated, forms yellow solutions with green fluorescence, is hydrolysed slowly by boiling aqueous potassium hydroxide forming the triether, and becomes brownish-violet on treatment with concentrated sulphuric acid; (*b*) the *penta-acetyl* derivative of the triether, $C_{86}H_{62}O_{14}$, is obtained on evaporation of the ethereal washings from the anhydro-compound and crystallisation from alcohol as a brown powder; (*c*) the $2^{\mathrm{I}}7^{\mathrm{I}}$-*anhydrohexa-acetyl* derivative of the diether, $C_{88}H_{64}O_{15},C_2H_6O$, separates from the alcoholic filtrate from the preceding substance on concentration at the laboratory temperature, sinters and swells up slightly at 115°, decomposes with effervescence above 160°, loses acetic anhydride and forms the brown tritanone ether on prolonged heating at high temperatures, and gives a brownish-violet coloration with concentrated hydrochloric or sulphuric acid.

Simultaneous reduction and acetylation of the acetoxy-diether-anhydride by boiling with sodium acetate, zinc dust, and acetic anhydride leads to the formation of the $2^{\mathrm{I}}7^{\mathrm{I}}$: $2^{\mathrm{II}}7^{\mathrm{II}}$: $2^{\mathrm{III}}7^{\mathrm{III}}$-*trianhydro-octa-acetyl* derivative of the octahydrodiether, $C_{92}H_{72}O_{15}$, which is obtained in two modifications; one of these is insoluble in cold ether and separates from a mixture of alcohol and benzene in colourless, spicular crystals, m. p. 174°. The second modification is soluble in cold ether and on evaporation of its ethereal-alcoholic solution separates as a white, granular mass, m. p. 104—105°, or after heating on the water-bath, 120—125°; when repeatedly dissolved in ether and evaporated with alcohol, it changes gradually into the first modification. In one experiment, a *product*, $C_{92}H_{74}O_{16}$, forming colourless crystals, m. p. 242°, was obtained. When distilled in a vacuum, the colourless isomerides decompose, forming diphenylmethane, acetic and benzoic acids, and a *substance* which crystallises from alcohol, m. p. about 135°, has a characteristic, aromatic odour, and dissolves in aqueous potassium hydroxide, forming a solution with blue fluorescence.

When boiled with alcoholic potassium hydroxide, all the acetyl derivatives described, with the exception of the diacetyl derivatives, dissolve, forming a bluish-red solution which has a green fluorescence and becomes colourless on dilution with water.

The following oxonium salts and derivatives are described :—Of the diacetyl-diether-anhydride : the *hydrochloride*, $C_{78}H_{54}O_{10},2HCl,H_2O$, crystallises in slender, yellow needles, and loses hydrogen chloride at about 200° ; the *sulphate*, $C_{78}H_{54}O_{10},2H_2SO_4,2H_2O$, forms microscopic, yellow leaflets, m. p. about 260° ; the *phosphate* forms a yellow powder ; the *picrate* forms yellow, microscopic, rhombic leaflets, m. p. 135—140° ; the *acetyl chloride* derivative forms an unstable, yellow, crystalline powder, and decomposes on the water-bath ; the *methyl sulphate* compound, $C_{78}H_{54}O_{10},SO_4Me_2$, forms a glistening, brownish-yellow, crystalline powder, the alcoholic filtrate from which deposits the methyl sulphate compound of the red tritanone ether in glistening, violet needles.

Derivatives of the triether : the *hydrochloride*, $C_{76}H_{52}O_9,3HCl$, forms transparent, brownish-yellow needles having a greenish-blue lustre ; the *sulphate*, $C_{76}H_{52}O_9,1\frac{1}{2}H_2SO_4$, crystallises in glistening, golden-yellow, quadratic leaflets ; the *phosphate* forms brownish-yellow, granular crystals ; the *acetyl chloride* derivative, $C_{76}H_{52}O_9,C_2H_3OCl$, forms a delicate, yellow, crystalline powder.

The anhydropenta-acetyl derivative of the triether forms a *hydrochloride*, $C_{86}H_{60}O_{18},3HCl$, crystallising in yellow needles or brown, rhombic leaflets, and a *sulphate*, $C_{86}H_{60}O_{18},2\frac{1}{2}H_2SO_4$, crystallising in brownish-yellow, rectangular rods.

The brown tritanone ether forms a *hydrochloride*, $C_{78}H_{48}O_7,2HCl$, and a brownish-violet *sulphate*, $C_{78}H_{48}O_7,H_2SO_4$, or in another preparation, $C_{78}H_{48}O_7,2H_2SO_4$.

The following are derivatives of the red tritanone ether : the *hydrochloride*, $C_{76}H_{48}O_7,2HCl$, *sulphate*, $C_{76}H_{48}O_7,H_2SO_4$, *phosphate*,

$$C_{76}H_{48}O_7,\tfrac{1}{2}H_3PO_4,$$

and *methyl sulphate* derivative, $C_{76}H_{48}O_7,SO_4Me_2$, crystallises in violet to violet-blue needles ; the *acetyl chloride* derivative,

$$C_{76}H_{48}O_7,2C_2H_3OCl,$$

separates from alcohol as a bluish-black, granular powder.

The oxonium salts are decomposed by cold alcoholic potassium hydroxide or by boiling water ; the acetyl chloride and methyl sulphate derivatives are attacked by cold water. G. Y.

Fission by Means of Hydrogen Chloride. **Felix Herrmann** (*Ber.*, 1906, **39**, 3812—3816. Compare Abstr., 1905, i, 733).—It has been shown previously that the oxidation which takes place during the formation of complex organic auric compounds such as aurodibenzylsulphine chloride and auric dibenzyl sulphide dichloride and leads to the formation of dibenzylsulphine oxide is a reversible reaction. Similarly, the action of hydrogen chloride on aurodibenzylsulphine chloride and diphenylsulphine oxide in chloroform solution leads to the formation of the sparingly soluble *auric* compound, $S(C_7H_7)_2AuCl_2$, and diphenyl sulphide. Other readily oxidisable substances are not oxidised in this manner.

The action of hydrogen chloride on 3 mols. of dibenzylsulphine oxide in chloroform solution in the absence of the gold compound, leads to the formation of 2 mols. of benzaldehyde and 1 mol. each of dibenzyl disulphide, dibenzyl sulphide, and water. If the action of the hydrogen chloride is prolonged, absorption takes place, the temperature rises to 40°, and after some time the contents of the flask boil suddenly with escaping hydrogen chloride and become turbid in consequence of the formation of water. The products of the reaction are then benzaldehyde, dibenzyl disulphide, water, and small amounts of benzyl chloride. The intermediate labile *additive* product of dibenzylsulphine oxide and hydrogen chloride, isolated by cooling the reacting mixture with ice, crystallises in white needles and in the absence of moisture remains unchanged for long periods. G. Y.

Transformation of Cinnamyl Alcohol into Phenylpropylene (Allylbenzene) and Phenylpropyl Alcohol by Metal ammoniums. E. CHABLAY (*Compt. rend.*, 1906, **143**, 829—831. Compare Abstr., 1905, i, 503).—Cinnamyl alcohol is reduced by sodium ammonium at −80° to form a small quantity of phenylpropylene (allylbenzene), b. p. 165—170°, yielding a dibromo-derivative, m. p. 67° (Fittig gives 66·5°, Abstr., 1874, 894, and Senfter and Tafel give 65—66°, Abstr., 1894, i, 580), but the chief product of the reduction is γ-phenylpropyl alcohol (compare Fittig, Abstr., 1873, 899; and Rügheimer, Abstr., 1874, 894), which forms a viscous, colourless, fragrant liquid, b. p. 236—237°/750 mm., D^{18} 1·007 (Rügheimer gives 1·008), does not solidify in solid carbon dioxide, and on oxidation forms phenylpropionic acid, m. p. 47·5°. M. A. W.

Benzoyl Nitrate. FRANCIS E. FRANCIS (*Ber.*, 1906, **39**, 3798—3804).—This is an amplification of work previously described (Trans., 1906, **89**, 1). As prepared, benzoyl nitrate always contains 15—20 % of benzoic anhydride, and has D_0^0 1·3.

Butyryl nitrate is a light yellow liquid which detonates when heated.

Benzoyl nitrate reacts readily with thiophen, *m*-xylene, mesitylene, anisole, phenetole, or veratrole, forming *o*-nitro-derivatives; in some cases dilution with carbon tetrachloride is necessary. The reaction takes place less easily with bromobenzene, benzoyl chloride, or benzoyl cyanide, only traces of the *p*-nitro-derivatives being obtained. With α- and β-naphthol, 2 : 4-dinitro-α-naphthol and 1 : 6-dinitro-β-naphthol respectively are formed; better yields are obtained with α-naphthol ethyl ether, which yields the 4-nitro- with only traces of the 1 : 2-dinitro-derivative, and β-naphthol methyl and ethyl ethers which yield the corresponding 1-nitro-derivatives.

Benzaldehyde, anisaldehyde, salicylaldehyde, and *o*-methoxybenzaldehyde are oxidised by benzoyl nitrate, forming the corresponding acids; only with anisaldehyde and salicylaldehyde are traces of nitro-derivatives obtained. Mandelonitrile is readily converted into the *nitro*-derivative, $NO_2\cdot CPh(OH)\cdot CN$, m. p. 77—78°, and is decomposed by water or alkali hydroxides, forming benzoic, nitrous, and hydrocyanic acids.

3-Nitrovanillin, 5-nitrocoumarin, and a dinitro-β-naphtholaldehyde, m. p. 194—195°, are formed quantitatively by the action of benzoyl nitrate on vanillin, coumarin, and β-naphtholaldehyde respectively, whilst piperonal forms only small amounts of 6-nitropiperonal, being simultaneously oxidised.

In some cases, benzoyl nitrate acts as an oxidising agent; thiophenol is oxidised to diphenyl disulphide, hydrazobenzene to azobenzene.

G. Y.

Reactions of Benzoyl Nitrate with Amines. THOMAS H. BUTLER (*Ber.*, 1906, **39**, 3804—3807. Compare Francis, Trans., 1906, **89**, 1; and preceding abstract).—Benzoyl nitrate reacts with primary aromatic amines, *m*-chloroaniline, *p*-chloroaniline, *m*-nitroaniline, *p*-anisidine, *o*-toluidine, and 1 : 3 : 4-xylidine, to form the substituted anilides together with the nitrate of the base. Phenylhydrazine forms *s*-benzoylphenylhydrazine. The secondary bases of the fatty series react with benzoyl nitrate in the same manner, forming disubstituted benzamides.

Benzoyldiamylamine is obtained as an oil, b. p. 300—319°, which is hydrolysed by concentrated hydrochloric acid, yielding benzoic acid and diamylamine hydrochloride.

The action of benzoyl nitrate on diphenylamine leads to the formation of only a small amount of benzodiphenylamide, or on ethylaniline to impure phenylethylnitroamine, whilst with methyl-*p*-toluidine, *p*-tolylmethylnitroamine, $C_7H_7\cdot NMe\cdot NO_2$, is formed in almost quantitative yields. When treated with concentrated sulphuric and glacial acetic acids, this is converted into 3-nitro-4-methylaminotoluene.

The action of benzoyl nitrate on acetanilide in carbon tetrachloride solution at low temperatures leads to the formation of a small amount of a white, crystalline *substance* which may be the nitroamine, $NO_2\cdot NPhAc$; it explodes violently if rubbed when dry, and gradually changes into *o*-nitroacetanilide; this is formed also if the action of benzoyl nitrate on acetanilide takes place at a slightly higher temperature.

o-Nitrophenacetin is obtained without formation of an explosive intermediate compound when phenacetin is treated with benzoyl nitrate in carbon tetrachloride solution.

G. Y.

Action of Ammonium Sulphide on *aa*-Dichloroamides and on *a*-Ketoamides. CELSO ULPIANI and G. CHIEFFI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 511—516. Compare Ulpiani and Ciancarelli, Abstr., 1904, i, 162).—Although hydrogen sulphide acts on *a*-ketoamides giving trithiodiamides (*loc. cit.*), it does not react with the similarly constituted *aa*-dichloroamides, probably on account of the hydrogen chloride formed. With ammonium sulphide, however, *aa*-dichloroamides give pentathiotetramides, $S(S\cdot CHR\cdot CO\cdot NH_2)_4$. This reaction takes place in two stages, the action of hydrogen sulphide on the *aa*-dichloroamide forming trithiodiamide, which is converted into pentathiotetramide by ammonia.

Pentathiotetraphenylacetamide, $S(S\cdot CHPh\cdot CO\cdot NH_2)_4$, prepared by the interaction of ammonium sulphide and *αα*-dichlorophenylacetamide or of ammonia and trithiodiphenylacetamide or of ammonium sulphide and benzoylformamide, crystallises with $2H_2O$ in microscopic, rectangular plates, m. p. 235°.

Pentathiotetracetamide, $S(S\cdot CH_2\cdot CO\cdot NH_2)_4$, obtained by the action of ammonium sulphide on dichloroacetamide, separates from water in crystals, m. p. 146—148°.

Pentathiotetrapropionamide, $S(S\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2)_4$, prepared from ammonium sulphide and *αα*-dichloropropionamide, crystallises from alcohol or water in rectangular plates, m. p. 187—188°.

When heated with a solution of potassium hydroxide (6 mols.), (1) pentathiotetraphenylacetamide yields a *substance*,

$$C_{16}H_{14}O_4S_2,2H_2O,$$

m. p. 215°, forming microscopic, elongated, rectangular crystals; (2) pentathiotetraglycollamide, a substance which, on oxidation with ferric chloride, gives dithioglycollic acid; and (3) pentathiotetrapropionamide, which, with ferric chloride, yields dithiolactic acid. T. H. P.

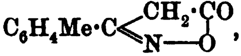
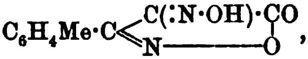
Velocity of the Addition of Bromine to Cinnamic Acid.

WALTER HERZ and BRUNO MYLIUS (*Ber.*, 1906, **39**, 3816—3820).—The authors propose to study the velocity of the addition of halogens to ethylene linkings, with special reference to the influence of various solvents and of catalysts, and finally to investigate from a chemical physical standpoint the usual "addition of iodine" method of estimating fats.

The results of two series of experiments in which cinnamic acid was heated with pure bromine in chloroform solution at 25°, in the second series with addition of bromoform, when calculated for a bimolecular reaction gave satisfactorily steady constants. Iodine, if present, acts as a catalytic agent as the constant is greatly increased, being about ten times as large with 0·0102 gram of iodine for 2·0235 millimols. of cinnamic acid. In this case the constant decreases markedly with the time, in consequence probably of the formation of di-iododihydrocinnamic acid taking place in presence of bromine. This decrease of the constant becomes more marked in experiments with large proportional quantities of iodine. With impure bromine, the value of the velocity constant is less steady, pointing to by-reactions, and is three to four times as large; the increase in the value of the constant is still greater, as are also its variations, when "technical" bromine is employed. In all these experiments the first value for the velocity is unsatisfactory.

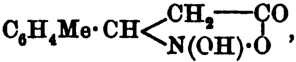
With carbon tetrachloride as solvent, a constant of higher value but less steadiness is obtained. G. Y.

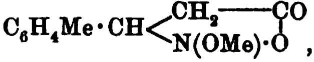
Unsaturated Compounds. III. Addition of Free Hydroxylamine to Homologues of Cinnamic Acid. Constitution of and Derivatives of β-Hydroxylamino-β-p-tolylpropionic Acid.

THEODOR POSNER and H. OPPERMANN (*Ber.*, 1906, **39**, 3705—3713. Compare Abstr., 1904, i, 160; Abstr., 1906, i, 955).—*β-Hydroxylamino-β*-p-*tolylpropionic acid*, $C_6H_4Me\cdot CH(NH\cdot OH)\cdot CH_2\cdot CO_2H$, obtained by the action of hydroxylamine on *p*-methylcinnamic acid, crystallises in leaflets, m. p. 195°. In the cold it reduces both Fehling's solution and ammoniacal silver nitrate; it forms a *diacetyl derivative*, $C_6H_4Me\cdot CH(NAc\cdot OAc)\cdot CH_2\cdot CO_2H$, m. p. 194°. When acted on by ammoniacal silver nitrate the acid forms 3-p-*tolyl*iso*oxazole*-5-*one*,  $C_6H_4Me\cdot C{<}\begin{array}{l}CH_2\cdot CO\\ N\text{———}O\end{array}$, which separates from light petroleum in silky needles, m. p. 133°. It is readily soluble in sodium carbonate and in alkalis and is reprecipitated by acids. Its constitution is determined by its behaviour with nitrous acid when 4-iso*nitroso*-3-p-*tolyl*iso*oxazole*-5-*one*,  $C_6H_4Me\cdot C{<}\begin{array}{l}C(:N\cdot OH)\cdot CO\\ N\text{—————}O\end{array}$, is formed.

β-*Ethoxylamino*-β-p-*tolylpropionic acid*,
$C_6H_4Me\cdot CH(NH\cdot OEt)\cdot CH_2\cdot CO_2H$,
prepared by alkylating β-hydroxylamino-β-*p*-tolylpropionic acid with ethyl alcohol and hydrochloric acid, separates from light petroleum in colourless needles, m. p. 87°. The alkyl group is readily eliminated by the addition of potassium hydroxide. The acid readily reduces Fehling's solution and ammoniacal silver nitrate, and is converted by the latter into the *p*-tolyl*iso*oxazolone.

β-*Methoxylamino*-β-p-*tolylpropionic acid*,
$C_6H_4Me\cdot CH(NH\cdot OMe)\cdot CH_2\cdot CO_2H$,
separates from light petroleum in colourless needles, m. p. 92°.

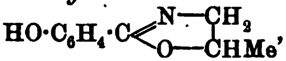
β-*Nitrosohydroxylamino*-β-p-*tolylpropionic acid*,
$C_6H_4Me\cdot CH[N(OH)\cdot NO]\cdot CH_2\cdot CO_2H$,
m. p. 122°, is obtained by the action of nitrous acid on β-hydroxylamino-β-*p*-tolylpropionic acid. When its solution in benzene is heated, nitrous fumes are evolved and 2-*hydroxy*-3-p-*tolyl*iso*oxazolidone*,  $C_6H_4Me\cdot CH{<}\begin{array}{l}CH_2\text{——}CO\\ N(OH)\cdot O\end{array}$, m. p. 141°, is formed.

β-*Nitrosomethoxylamino*-β-p-*tolylpropionic acid*,
$C_6H_4Me\cdot CH[N(OMe)\cdot NO]\cdot CH_2\cdot CO_2H$,
m. p. 53°, is obtained by the action of nitrous acid on β-methoxylaminotolylpropionic acid. It readily decomposes with the formation of 2-*methoxy*-3-p-*tolyl*iso*oxazolidone*,  $C_6H_4Me\cdot CH{<}\begin{array}{l}CH_2\text{———}CO\\ N(OMe)\cdot O\end{array}$, which melts at 118°.

β-*Amino*-β-p-*tolylpropionic acid* (β-*amino*-p-*methylhydrocinnamic acid*), $C_6H_4Me\cdot CH(NH_2)\cdot CH_2\cdot CO_2H$, obtained by the prolonged boiling of an alcoholic solution of β-hydroxylamino-γ-*p*-tolylpropionic acid with free hydroxylamine, crystallises in leaflets, m. p. 226°. Its *copper* salt crystallises with $4H_2O$. The *benzoyl* derivative separates from alcohol in leaflets, m. p. 210°.

β-*Carbamido*-β-p-*tolylpropionic acid*,
$C_6H_4Me\cdot CH(NH\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2H$,
m. p. 210°, is converted by the action of nitrous acid into β-*hydroxy*-β-p-*tolylpropionic acid*, $C_6H_4Me\cdot CH(OH)\cdot CH_2\cdot CO_2H$, m. p. 185°, which forms a *barium* salt containing $1H_2O$. A. McK.

Acylated Allylamines. OTTO DIELS and ERICH BECCARD (*Ber.*, 1906, **39**, 4125—4132. Compare Kay, Abstr., 1894, i, 76).—*Salicylallyl*-

amide, $HO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2$, formed by heating salicylic acid with allylthiocarbimide at 140° for twenty hours, crystallises from light petroleum in long needles, m. p. 52° (corr.). The aqueous solution, which has acid properties, gives with ferric chloride a violet coloration. The *dibromide* crystallises from ethyl acetate in slender, white needles, m. p. 187° (corr.), but is decomposed by hot methyl or ethyl alcohol. When salicylallylamide is heated with hydrochloric acid at 100° under pressure, the *hydrochloride* of 2-o-*hydroxyphenyl-5-methyl*-4 : 5-*dihydro-oxazole*,  $HO{\cdot}C_6H_4{\cdot}C{<}\begin{matrix}N{-}CH_2\\O{-}CHMe\end{matrix}$, is formed, and is precipitated from its alcoholic solution by ether in slender, white needles, m. p. 161° (corr.). The *potassium* salt crystallises in compact, white needles, and the *platinichloride* in fine, yellow leaflets. The *base* is a yellow oil with a characteristic faint odour.

Hippurallylamide, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2$, prepared by heating allylthiocarbimide and the corresponding acid at 130° for six hours, crystallises from acetone in aggregates of small, white, irregular plates, m. p. 138·5° (corr.). The *hydrobromide*, $C_{12}H_{14}O_2N_2,HBr$, precipitated either by mixing acetic acid solutions of hydrogen bromide and amide, or by passing the gas through a chloroform solution of the amide, forms white crystals, m. p. 140°, unstable in moist air and completely decomposed by water into its components. *Hippuro-β-bromopropylamide*, prepared by heating the amide in a saturated solution of hydrogen bromide in acetic acid under pressure at 60°, crystallises from ethyl acetate in rectangular plates, m. p. 128° (corr.). The *hippurodibromopropylamide*, m. p. 121° (corr.), crystallises from acetone in short, compact needles. *Hippurobromoallylamide*,

$$NHBz{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CBr{:}CH_2,$$

m. p. 167° (corr.), formed by heating sodium ethoxide and the dibromide on the water-bath, separates from alcohol in slender, white plates. The benzoylglycylglycine (m. p. 206°) first described by Curtius (Abstr., 1881, 1144) is obtained in good yield when a paste of hippurobromoallylamide in water is treated with ozone at 40—50° (compare also E. Fischer, Abstr., 1905, i, 263). W. R.

Carbon Monoxide Scission from Ethyl α-Bromo-α-phenylacetoacetate. OTTO DIMROTH and MAX EBLE (*Ber.*, 1906, **39**, 3928—3929. Compare Abstr., 1903, i, 631).—Just as ethyl α-bromopropionylphenylacetate, when distilled with steam, is converted into methylatropic acid, hydrogen bromide, and carbon monoxide, ethyl α-bromo-α-phenylacetoacetate undergoes decomposition into ethyl atropate, hydrogen bromide, and carbon monoxide. The latter action, which does not, however, take place with the same ease as the former, is represented by the equation

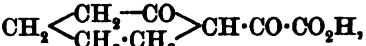
$$CH_3{\cdot}CO{\cdot}CBrPh{\cdot}CO_2Et = CH_2{:}CPh{\cdot}CO_2Et + CO + HBr.$$

1-*Phenyltetronic acid* is contained in the residue from the distillation in steam; it separates from dilute alcohol in leaflets, m. p. 254°. Its constitution was established by boiling it with baryta when phenylacetic acid and glycollic acid were formed. A. McK.

Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. IV. Synthesis of 1-*iso*Propyl*cyclo*hexane-2-one and of *m*-Menthane-2-one from *cyclo*Hexanone.

Arthur Kötz and A. Michels (*Annalen*, 1906, **350**, 204—216. Compare Abstr., 1906, i, 667).—Instances are given of steric hindrance in the formation of the semicarbazones of *cyclo*hexanones and of their carboxylic esters.

Ethyl *cyclo*hexane-2-one-1-carboxylate is obtained from *cyclo*hexanone, sodium ethoxide, and ethyl oxalate (compare Dieckmann, Abstr., 1901, i, 539).

cyclo*Hexane-2-one*-1-*oxalic acid*, 

$CH_2<\begin{matrix}CH_2—CO\\CH_2·CH_2\end{matrix}>CH·CO·CO_2H$,

obtained from the initial product of condensation in the preceding reaction, m. p. 121°, dissolves in water; the *ethyl* ester has b. p. 165°/17 mm.

Ethyl 1-*methyl*cyclo*hexane-2-one*-1-*carboxylate*, b. p. 113°/11 mm., prepared from methyl iodide and ethyl sodio*cyclo*hexane-2-one-1-carboxylate, forms a *semicarbazone*, m. p. 152°.

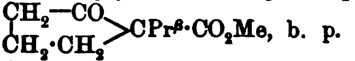
Ethyl 1-iso*propyl*cyclo*hexane-2-one*-1-*carboxylate*, prepared in a similar manner, has b. p. 132°/15 mm., and forms a *semicarbazone*, m. p. 151°.

1-iso*Propyl*cyclo*hexane-2-one*, obtained from the preceding ester and methyl alcoholic potash, is a colourless liquid with the odour of menthone, b. p. 92°/15 mm.; it forms an additive compound with sodium hydrogen sulphite and a *semicarbazone*, m. p. 187°.

Ethyl 1-*methyl*cyclo*hexane-2-one*-1:3-*dicarboxylate*, b. p. 160°/10 mm., prepared from sodium ethoxide, ethyl oxalate, and ethyl 1-methyl*cyclo*hexane-2-one-1-carboxylate, forms a *semicarbazone*, m. p. 239°.

Ethyl 3-iso*propyl*-1-*methyl*cyclo*hexane-2-one*-1:3-*dicarboxylate*, obtained from the sodium derivative of the preceding compound and *iso*propyl iodide, is a colourless and odourless liquid, b. p. 165°/10 mm., does not form a semicarbazone, and by boiling methyl alcoholic potash is converted into *m*-menthane-2-one (Abstr., 1906, i, 666). C. S.

Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. V. Synthesis of 1-Methyl-3-*iso*propyl*cyclo*pentane-2-one (Dihydrocamphophorone or Dihydropulegone) from Ethyl *cyclo*Pentane-2-one-1-carboxylate.

Arthur Kötz and Paul Schüler (*Annalen*, 1906, **350**, 217—228).—Methyl *cyclo*pentane-2-one-1-carboxylate, obtained by Dieckmann's method (Abstr., 1901, i, 539), is converted into the metallic derivative by treatment with potassium and sodium in xylene, then treated with 100 % excess of *iso*propyl iodide and heated at 130—140° for thirty-five hours, when it gives a 55 % yield of *methyl* 1-iso*propyl*cyclo*pentane-2-one*-1-*carboxylate*, 

$\begin{matrix}CH_2—CO\\|\\CH_2·CH_2\end{matrix}>CPr^{\beta}·CO_2Me$,

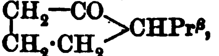
b. p. 112°/11 mm., which does not give a coloration with ferric chloride, and forms a *semicarbazone*, m. p. 193—194°. The corresponding *ethyl* ester has b. p. 119°/12 mm.

Methyl α-iso*propyladipate*, b. p. 132—133°/15 mm., is obtained from the preceding methyl ester and sodium methoxide; treatment with sodium leads to the formation of *methyl* 3-iso*propyl*cyclo*pentane-2-one*-1-*carboxylate*, b. p. 116—125°/11 mm., which forms a *semicarb-*

azone, m. p. 134—135°. The corresponding *ethyl* ester has b. p. 128—129°/12 mm.

Ethyl 1-*methyl*-3-iso*propyl*cyclo*pentane-2-one*-1-*carboxylate*, b. p. 130—135°/12 mm., obtained from the metallic derivatives of the preceding ester and methyl iodide, does not give a blue coloration with ferric chloride.

By treatment with barium hydroxide, ethyl 1-*iso*propyl*cyclo*pentane-2-one-1-carboxylate yields iso*propyl*cyclo*pentane*-2-one,



$$\begin{array}{l}CH_2{-}CO\\ CH_2\cdot CH_2\end{array}\!\!>CHPr^{\beta},$$

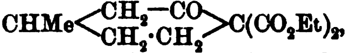
b. p. 175—176°, which forms a *semicarbazone*, m. p. 183—184°.

1-Methyl-3-*iso*propyl*cyclo*pentane-2-one (dihydrocamphorphorone or dihydropulegone) (compare Semmler, Abstr., 1902, i, 385; Wallach, Abstr., 1903, i, 567), b. p. 181—186°, is obtained in a similar manner to the preceding ketone, and forms a *semicarbazone*, m. p. 193—194·5°.

C. S.

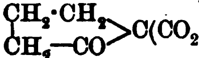
Syntheses by Means of the Carboxylic Esters of Cyclic Ketones. VI. Dicarboxylic Esters of Cyclic Monoketones.

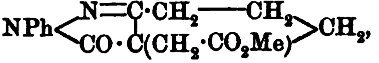
ARTHUR KÖTZ (*Annalen*, 1906, **350**, 229—246).—[With ALBERT HARZER.]—*Ethyl* 1-*methyl*cyclo*hexane*-3-*one*-4-*dicarboxylate*,



$$CHMe\!<\!\begin{array}{l}CH_2{-}CO\\ CH_2\cdot CH_2\end{array}\!\!>C(CO_2Et)_2,$$

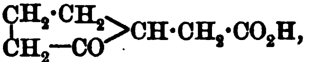
obtained from ethyl chlorocarbonate and ethyl sodio-1-methyl*cyclo*hexane-3-one-4-carboxylate, is a yellow oil, b. p. 232°/17 mm. and 221°/11 mm., does not form a semicarbazone, and yields with phenylhydrazine, Hesse's pyrazolone derivative, m. p. 242°. The ester is decomposed by concentrated sodium hydroxide into 3-methyl*cyclo*hexane-1-one.

[With PAUL SCHÜLER.]—*Ethyl* cyclo*pentane*-2-*one*-1-*acetate*-1-*carboxylate*,  $\begin{array}{l}CH_2\cdot CH_2\\ CH_2{-}CO\end{array}\!\!>C(CO_2Et)\cdot CH_2\cdot CO_2Et$, b. p. 162—163°/14 mm., obtained from ethyl bromoacetate and ethyl *cyclo*pentane-2-one-1-carboxylate, does not give a blue coloration with alcoholic ferric chloride, and forms a *semicarbazone*, m. p. 148—149°. The corresponding *methyl* ester, b. p. 153—154°/12 mm. and 157—158/17 mm., forms a *semicarbazone*, m. p. 180—181°. The methyl ester reacts with methyl-alcoholic ammonia to form the *amide*, $C_8H_{12}O_3N_2$, m. p. 162—163°, and with phenylhydrazine to form a *pyrazolone* derivative,



$$NPh\!<\!\begin{array}{l}N{=}C\cdot CH_2{-\!-}CH_2\\ CO\cdot C(CH_2\cdot CO_2Me)\end{array}\!\!>CH_2,$$

m. p. 146—147°.

cyclo*Pentane*-2-*one*-1-*acetic acid*,  $\begin{array}{l}CH_2\cdot CH_2\\ CH_2{-}CO\end{array}\!\!>CH\cdot CH_2\cdot CO_2H$, m. p. 50—51°, is prepared by hydrolysing ethyl *cyclo*pentane-2-one-1-carboxylate-1-acetate with hydrochloric acid. By esterification with alcohol and hydrogen chloride it yields the *ethyl* ester, b. p. 129—130°/18 mm., which has the odour of ethyl acetate, forms a *semicarbazone*, m. p. 173—174°, and by treatment with sodium yields *ethyl αγ-di*cyclo*pentane-2-one-acetoacetate*,

$$C_5H_7O\cdot CH_2\cdot CO\cdot CH(C_5H_7O)\cdot CO_2Et,$$

b. p. 240—260°/20 mm.; this forms a *semicarbazone*, m. p. 191—192°.

When ethyl *cyclo*pentane-2-one-1-carboxylate-1-acetate is heated with sodium ethoxide, it is converted into *ethyl pentane-αβε-tricarboxylate*, $C_{14}H_{24}O_6$, b. p. 188—189°/18 mm.; the *methyl* ester has b. p. 180—181°/18 mm. Hydrolysis of the esters by hydrochloric acid, followed by keeping in a vacuum over sulphuric acid, yields an *anhydride*, $C_8H_{10}O_5$, m. p. 95°, which by treatment with water yields the *acid*, $C_8H_{12}O_6$, m. p. 81—84°.

[With ARTHUR BIEBER.]—*Ethyl 1-methyl*cyclo*hexane-3-one-4-carboxylate-4-acetate*, b. p. 194—195°/12 mm., is obtained from ethyl sodio-1-methyl*cyclo*hexane-3-one-4-carboxylate and ethyl chloro- or bromoacetate; the *semicarbazone* has m. p. 126—127°.

[With GUSTAV KAYSER.]—*Ethyl 1-methyl*cyclo*hexane-3-one-4-acetate*, b. p. 145—155°/0 mm., is obtained by hydrolysing the preceding ester and esterifying the resulting acid, and forms a *semicarbazone*, m. p. 116°.

Ethyl β-methylhexane-αεζ-tricarboxylate, b. p. 215—218°/0 mm., obtained by decomposing ethyl 1-methyl*cyclo*hexane-3-one-4-acetate-4-carboxylate with sodium ethoxide; when hydrolysed, yields the *acid*, $C_{10}H_{16}O_6$, m. p. 120°. C. S.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XV. Esterification of 4-Nitrophthalic Acid. RUDOLF WEGSCHEIDER (*Monatsh.*, 1906, **27**, 777—779. Compare Wegscheider and Kailan, Abstr., 1906. ii, 340; Goldschmidt and Sunde, Abstr., 1906, ii, 219).—In view of the uncertainty attached to Goldschmidt's measurements of the velocity of esterification previously utilised (Wegscheider and Lipschitz, Abstr., 1901, i, 32; Wegscheider and Bondi, Abstr., 1905, i, 895) in the discussion of the esterification of 4-nitrophthalic acid, the esterification of *m*-nitrobenzoic acid by means of hydrogen chloride and alcohol has been repeated and found to take place more slowly than that of *p*-nitrobenzoic acid under similar conditions. This shows that the formation of 1-ethyl hydrogen 4-nitrophthalate, by partial hydrolysis of ethyl 4-nitrophthalate, and not that by esterification of 4-nitrophthalic acid with hydrogen chloride and alcohol, is the irregular action. G. Y.

Direct Comparison of the Diphenyladipic Acids with the Truxillic Acids. HEINRICH JESSEN (*Ber.*, 1906, **39**, 4089—4092).—As the two βγ-diphenyladipic acids obtained by Henle on reduction of methyl cinnamate (Abstr., 1906, i, 669) closely resemble the truxillic acids, the author has compared some derivatives of the βγ-diphenyladipic acid, which crystallises with C_2H_6O, m. p. 276° (270°, Henle, *loc. cit.*), with the corresponding derivative of α-truxillic acid, m. p. 274°, and found them not to be identical.

Methyl βγ-diphenyladipate, m. p. 173—174°, and methyl α-truxillate, m. p. 173—174°, give distinctly different figures on analysis. *Ethyl βγ-diphenyladipate*, $C_{22}H_{26}O_4$, crystallises in glistening prisms, m. p. 114°; ethyl α-truxillate, m. p. 146°. *Calcium βγ-diphenyladipate* $C_{18}H_{16}O_4Ca$, forms a delicate, crystalline precipitate; *calcium α-truxil-*

late, $C_{18}H_{14}O_4Ca,H_2O$, crystallises in needles. *Barium βγ-diphenyladipate*, $C_{18}H_{16}O_4Ba,3H_2O$, forms short, glistening prisms; *barium α-truxillate*, $C_{18}H_{14}O_4Ba,8\frac{1}{2}H_2O$, crystallises in large prisms which rapidly effloresce.

The action of concentrated nitric acid on βγ-diphenyladipic acid leads to the formation of two *dinitro*-derivatives, $C_{18}H_{16}O_8N_2$, m. p. 318° and 218° respectively. The latter dinitro-acid forms an *ethyl* ester, $C_{22}H_{24}O_8N_2$, which crystallises in light yellow needles, m. p. 169—172°. G. Y.

Derivatives of Truxillic Acid. Heinrich Jessen (*Ber.*, 1906, **39**, 4086—4089).—Homans, Stelzner, and Suckow's α-dinitro-α-truxillic acid (Abstr., 1891, 1495) is the *pp*-dinitro-acid, as the corresponding diamino-acid yields *p*-aminocinnamic acid when distilled.

Di-p-*acetylamino-α-truxillic acid*, $C_4H_4(C_6H_4{\cdot}NHAc)_2(CO_2H)_2$, prepared by boiling the diamino-acid with sodium acetate and acetic anhydride, crystallises in needles, m. p. 276°. *Ethyl di*-p-*amino-α-truxillate*, $C_4H_4(C_6H_4{\cdot}NH_2)_2(CO_2Et)_2$, formed by the action of ethyl iodide on the silver salt, crystallises in leaflets.

Di-p-*chloro-α-truxillic acid*, $C_4H_4(C_6H_4Cl)_2(CO_2H)_2$, prepared from diazotised di-*p*-amino-α-truxillic acid by Sandmeyer's reaction, is difficult to purify, m. p. about 278—280°.

Dinitrodi-p-*hydroxy-α-truxillic acid*, $C_4H_4[C_6H_3(NO_2){\cdot}OH]_2(CO_2H)_2$, obtained by treating the di-*p*-hydroxy-acid with concentrated nitric acid, dissolves in much hot alcohol and could not be crystallised. The *ethyl* ester, $C_{22}H_{22}O_{10}N_2$, crystallises in glistening needles, m. p. 294°.

The action of potassium nitrate on di-*p*-nitro-α-truxillic acid in hot concentrated sulphuric acid solution leads to the formation of *tetranitro-α-truxillic acid*, $C_4H_4[C_6H_3(NO_2)_2]_2(CO_2H)_2$, which crystallises in glistening, yellow prisms, m. p. 262°, and is stable towards potassium permanganate. The *ethyl* ester, $C_{22}H_{20}O_{12}N_4$, crystallises from alcohol in glistening, flat prisms or from acetone in aggregates of needles, m. p. 146°. *Tetra-amino-α-truxillic acid*, obtained by reduction of the tetranitro-acid by means of tin and hydrochloric acid, is isolated in the form of its *hydrochloride*, $C_{18}H_{20}O_4N_4,2HCl$; this crystallises in white, glistening needles. The *hydrochloride* of ethyl tetra-amino-α-truxillate, $C_{22}H_{28}O_4N_4,2HCl$, prepared by reduction of the tetranitro-ester, crystallises in delicate leaflets and is almost insoluble in all organic solvents.

The oxidation of the tetra-substitution products of α-truxillic acid leads to the formation of derivatives of benzoic acid or undefined resins, and not of tetramethylene derivatives. G. Y.

Hydramides. Artur Fürth (*Monatsh.*, 1906, **27**, 839—847. Compare Fulda, Abstr., 1903, i, 199; Ofner, Abstr., 1904, i, 818; Ott, Abstr., 1905, i, 376).—The formation of mixed hydramides by the expulsion of two of the aldehyde groups of a hydramide by another aldehyde failed, as the reaction continues to the complete substitution of the one aldehyde by the other.

Hydrobenzamide, m. p. 102° (110°, Laurent, *Annalen*, 1837, **21**, 130).

Trimethyl-*p*-amarine (Gattermann, Abstr., 1906, i, 589) crystallises with $\frac{1}{2}H_2O$, sinters at 119—120°, and, although a meniscus is formed at 126—127°, is not melted completely below 136°.

*Hydrotri-*p*-nitrobenzamide*, $C_{21}H_{15}O_6N_5$, prepared by the action of concentrated aqueous ammonia on *p*-nitrobenzaldehyde, is flocculent, darkens at 160—170°, and does not melt on further heating.

When boiled with *m*-nitrobenzaldehyde in ethereal solution in a reflux apparatus, hydrobenzamide, hydro-*p*-toluamide (Gattermann, *loc. cit.*), hydrosalicylamide, or hydroanisamide yields hydrotri-*m*-nitrobenzamide, $N_2(CH{\cdot}C_6H_4{\cdot}NO_2)_3$, m. p. 160° (Bertagnini, *Annalen*, 1851, **79**, 272).

Furfuraldehyde, piperonal, anisaldehyde, and salicylaldehyde do not react in this manner with hydrobenzamide or hydro-*p*-toluamide.

G. Y.

Leuco-derivatives of Hydroxy-ketones. Berthold König and Stanislaus von Kostanecki (*Ber.*, 1906, **39**, 4027—4031).—When benzoresorcinol (Abstr., 1894, i, 506) is methylated with 1 gram-mol. of methyl sulphate, it yields the *monomethyl ether*, (*2-hydroxy-4-methoxybenzophenone*), $COPh{\cdot}C_6H_3(OH)(OMe)$, m. p. 66°; with a large excess of methyl sulphate it yields 2 : 4-*dimethoxybenzophenone*, m. p. 87—88°, which may also be prepared from benzoyl chloride and resorcinol dimethyl ether. The leuco-derivative of the dimethoxy-compound is an oil.

3 : 4-Dimethoxybenzophenone (Brüggemann, Abstr., 1896, i, 356), m. p. 103—104°, when reduced with zinc dust and alcoholic potash yields 3 : 4-*dimethoxybenzhydrol*, $OH{\cdot}CHPh{\cdot}C_6H_3(OMe)_2$, which crystallises from dilute alcohol in colourless prisms, m. p. 99°.

3 : 4 : 3′ : 4′-*Tetramethoxybenzhydrol*, $C_{17}H_{20}O_5,H_2O$, m. p. 95°, obtained by reducing the corresponding ketone (this vol., i, 75), and dissolves in concentrated sulphuric acid to a magenta-red solution.

2 : 5 : 3′ : 4′-*Tetramethoxybenzophenone*, m. p. 101—102°, obtained from quinol dimethyl ether and veratroyl chloride; the corresponding *leuco*-compound has m. p. 132—133°.

2 : 4 : 3′ : 4′-*Tetramethoxybenzophenone*, m. p. 107°, prepared from veratroyl chloride and resorcinol dimethyl ether; its *leuco*-compound has m. p. 108°. The leuco-derivatives are readily oxidised to the ketones by means of cold chromic acid solution.

J. J. S.

Action of Hydroxylamine on Ketones of the Type, $CHR\!:\!CH{\cdot}CH\!:\!CH{\cdot}CO{\cdot}R$. Roberto Ciusa (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 455—459).—With cinnamylideneacetophenone, hydroxylamine gives mainly a hydroxylamineoxime derivative, whilst with cinnamylideneacetone it yields only the ordinary oxime (compare Harries, Abstr., 1904, i, 427; 1905, i, 245).

Hydroxylaminocinnamylideneacetophenoneoxime, which, according to Thiele's law, should have the structure

$$OH{\cdot}NH{\cdot}CHPh{\cdot}CH\!:\!CH{\cdot}CH_2{\cdot}CPh\!:\!N{\cdot}OH,$$

crystallises from alcohol in colourless needles, m. p. 161°; its acetic acid solution gives with concentrated nitric acid a green coloration with a blue fluorescence. On reduction with sodium and amyl alcohol it yields a product, the *benzoyl* derivative of which, $C_{17}H_{19}N_2Bz$, crystallises from alcohol in minute needles, m. p. 226°. T. H. P.

Synthesis of Euxanthone. FRITZ ULLMANN and LÉON PANCHAUD (*Annalen*, 1906, **350**, 108—117. Compare Graebe, Abstr., 1889, 886; von Kostanecki, Abstr., 1892, 504).—2:6-Dinitrotoluene is converted by a series of reactions into 2-*chloro*-6-*methoxybenzoic acid*, which forms white needles, m. p. 141°, and by heating with sodium phenoxide and copper at 180—190° yields 2-phenoxy-6-methoxybenzoic acid, which without being isolated is converted by warm concentrated sulphuric acid into 1-*methoxyxanthone*, m. p. 138°, which forms a blue, fluorescent solution in alcohol. 1-Hydroxyxanthone, m. p. 147°, and obtained from the methyl ether and aluminium chloride in toluene, is identical with Michael's salicylresorcinol ether (Abstr., 1884, 310).

Euxanthone dimethyl ether, m. p. 149·5°, obtained in a similar manner from chloromethoxybenzoic acid and sodium *p*-methoxyphenoxide, is identical with Graebe and Aders' ether obtained from natural euxanthone (Abstr., 1902, i, 42), and is converted by aluminium chloride in benzene or toluene into a substance having m. p. 240° and identical with euxanthone from natural sources. C. S.

Condensation of *o*- and *p*-Nitrobenzoyl Chloride and Acetylacetone. H. MECH (*Compt. rend.*, 1906, **143**, 751—753).—*Di*-p-*nitrobenzylacetylacetone*, $C(COMe)_2(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, obtained by the action of sodioacetylacetone and *p*-nitrobenzyl chloride in absolute alcoholic solution, is a crystalline powder, m. p. 229°. From the mother liquor of the preceding preparation, δ-p-*nitrophenyl*-β-*butanone*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, can be isolated; it forms long, colourless, thin needles, m. p. 40—41°, and is probably formed by the hydrolysis of a monosubstituted derivative of acetylacetone,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(COMe)_2 + NaOH = MeCO_2Na + NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}COMe;$$

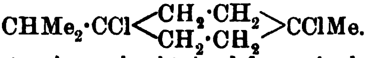
the *oxime*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}NOH$, crystallises in needles, m. p. 120°, reduces Fehling's solution and again yields the ketone when dissolved in hydrochloric acid.

Di-o-nitrobenzylacetylacetone, prepared similarly to the para-compound, forms prismatic crystals, m. p. 123°. M. A. W.

Oxidations with Silver Peroxide. III. Oxidation of *p*-Benzoquinone. R. KEMPF (*Ber.*, 1906, **39**, 3715—3727. Compare Abstr., 1906, ii, **24**, 25).—When *p*-benzoquinone is oxidised by silver peroxide, maleic acid and carbon dioxide are the main products, whilst formic acid and carbon monoxide are formed in smaller amounts. When maleic acid itself was oxidised, carbon dioxide was formed together with traces of formic acid, but mesotartaric acid was not detected.

The mechanism of the oxidation of *p*-benzoquinone is discussed. The quantitative methods, by which the proportions of the various oxidation products were estimated, are described. *p*-Benzoquinone and quinol are much more readily oxidised by silver peroxide than by sodium or ammonium persulphate. A. McK.

Terpenes and Ethereal Oils. LXXXII. Compounds, Purification, and Constitution of Terpinene. Otto Wallach (*Annalen*, 1906, **350**, 141—179).—Terpinene forms crystalline additive compounds with 2 mol. of halogen acid which exist in *cis*- and *trans*-modifications; the former has the lower melting point and has not been examined further. The *trans*-isomeride is best obtained from sabinene or the terpineol in majorana oil, or less readily from the crude terpinene resulting from the action of dilute sulphuric acid on terpine hydrate. The *hydrochloride*, $C_{10}H_{16},2HCl$, has m. p. 51—52°, the *hydrobromide*, 58—59°, and the hydriodide, 76°. These constants are very near those of the corresponding dipentene derivatives; the method of "mixed" melting points is employed to ascertain whether a halogen compound belongs to the terpinene or to the dipentene series. To the former is ascribed the constitution



$$\mathrm{CHMe_2{\cdot}CCl}<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CClMe}.$$

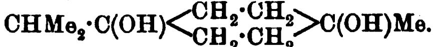
Chemically pure terpinene is obtained from the hydrochloride or the hydrobromide by means of aniline, b. p. 179—181°, D^{20} 0·846, n_D 1·4789.

Most carefully purified dipentene has b. p. 178—180°, which is somewhat higher than that of the active limonenes, a fact which requires further investigation.

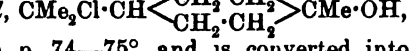
When terpinene dihydrobromide is treated at 0° with silver acetate in glacial acetic acid, α-terpineol and *cis*- and *trans*-terpines, m. p. 117° and 156—157° respectively, are obtained; this indicates that the terpinene compound has changed completely in the acetic acid solution into dipentene dihydrobromide.

[With Friedrich Boedecker.]—The following hydrochlorides were treated with excess of 2 % aqueous potash at 50—60°. Active limonene hydrochloride yields active α-terpineol. *trans*-Dipentene dihydrochloride yields dipentene, α-terpineol, *cis*- and *trans*-terpines; the method is very convenient for the preparation of the last-mentioned substance. *cis*-Dipentene dihydrochloride yields the same products as its isomeride with the exception of *trans*-terpine.

Terpinene dihydrochloride, after fifteen hours the temperature being raised to 100°, yields terpinene, α-terpineol, *cis*- and *trans*-terpine, and a *terpineol* and a *terpine*. The terpineol, $C_{10}H_{18}O$, b. p. 90°/11 mm. and 212—214°/760 mm., D 0·9290, n_D 1·4803, and differs from other terpineols in its less pleasant odour and in its combination with hydrogen chloride to re-form terpinene dihydrochloride. The terpine, $C_{10}H_{18}(OH)_2$, is more soluble than the isomerides, separates from ethyl acetate and light petroleum in glistening leaflets, m. p. 136·5—137·5°, and forms terpinene dihydrobromide with hydrogen bromide in glacial acetic acid. It is represented by the formula $\mathrm{CHMe_2{\cdot}C(OH)}<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{C(OH)Me}$.



With halogen acids, terpineols behave as follows: α-terpineol (Δ^1-menthene-8-ol), whether active or inactive, yields the dipentene derivative; β-terpineol ($\Delta^{8(9)}$-menthene-1-ol) yields the same and also 8-*chloromenthane*-1-*ol*, $\mathrm{CMe_2Cl{\cdot}CH}<\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CMe{\cdot}OH}$, which crystallises in needles, m. p. 74—75°, and is converted into *cis*-terpine by 2 %



aqueous potash ; γ-terpineol ($\Delta^{4(8)}$-menthene-1-ol) yields the dihydrochlorides of dipentene and of terpinene (compare Baeyer, Abstr., 1894, i, 252). To separate this mixture, it is shaken at 50° for two hours with 2°/₀ aqueous potash, whereby the dipentene dihydrochloride is converted into dipentene and α-terpineol.

Sabinene is converted into *trans*-terpinene dihydrohalide by halogen acids in glacial acetic acid (contrast Kondakoff and Skworzoff, Abstr., 1904, i, 438) and into terpinene by boiling dilute sulphuric acid. α-Thujene is also converted into the dihalide compounds of terpinene by halogen acids (contrast Kondakoff and Skworzoff (*loc. cit.*) ; Tschugaeff, 1904, i, 515).

Cardamom and majorana oils each contain the terpineol of the terpinene series, which by oxidation by 1°/₀ solution of potassium permanganate yields a *glycerol*, $C_{10}H_{17}(OH)_3$, m. p. 114—116°, $[\alpha]_D^{22}$ +21—24°, containing water of crystallisation which is lost at 130°, the residue subliming in crystals and having m. p. 129°, and is not oxidised by chromic acid to a keto-lactone.

When terpinene nitrosite is treated with an equivalent quantity of sodium methoxide or ethoxide, or alcoholic or aqueous potash, the alkali nitrite is formed together with a *substance*, $C_{20}H_{31}O_4N_3$, which separates from acetone and water in needles, is insoluble in acids or alkalis, has m. p. 163—164°, and forms a *benzoyl* derivative,

$$C_{20}H_{30}O_4N_3(COPh),$$

m. p. 127° (compare Semmler, Abstr., 1901, i, 330).

The paper concludes with a brief discussion on the constitution of terpinene. C. S.

Essential Oils. Heinrich Haensel (*Chem. Centr.*, 1906, ii, 1495—1496 ; from *Geschäftsber.*, April—Sept. 1906. Compare Abstr., 1906, i, 524).—The leaves and flowers of the alpine rose yield 0·123°/₀ of a yellow oil with a pungent, aromatic odour ; it has D^{18} 0·8620 and $\alpha_D^{16·5}$ − 4·33° ; the woody stems of the plant give 0·0097°/₀ of the same oil. The terpene, described by Wolpian as hydrocuminene, which occurs together with cymene in cumin oil, has D >0·880, and does not yield a crystalline nitrosochloride, hydrochloride, or hydrobromide. The fruit of a species of *Heracleum* known as "semence de panais" yields 1·7°/₀ of a greenish-yellow oil of an unpleasant odour having D^{20} 0·8508, $\alpha_D^{21·5}$ − 0·19°, acid number 1·3, and saponification number 228·1 ; the chief alcoholic constituent of this oil is octyl alcohol. *Laserpitium oil*, obtained in 1·87°/₀, yield from the fruits of a plant belonging to that genus, is a dark green oil with an odour resembling that of aniseed and caraway, it has D^{20} 0·9538, acid number 3·2, saponification number before acetylation 15·5, and 28·5 after ; it contains limonene, eugenol or dihydroeugenol methyl ether, and a paraffin, m. p. 57—58°. *Oil of rue* on saponification with alkali yields formic and butyric acids. *Sandal oil*, obtained from African sandal wood, is a brown oil of D^{20} 0·9589, $[\alpha_D]$ − 40·6°, acid number 1·7, saponification number 17·9, or after acetylation 88·3 ; it contains a sesquiterpene of b. p. 260—261·5°, D^{20} 0·9238, α_D^{18} − 39·62°, which does not give a solid hydrochloride. The oil, after saponification and drying, condenses with phenylcarbimide, forming diphenylcarbamide, but does not react in benzene solution with phthalic anhydride. The leaves of *Cyclopia genistoides* on distillation give 0·101% of a light brown, strongly smelling oil having D^{15} 0·8737 and $\alpha_D + 0·36°$ (in 10% solution in benzene); at ordinary temperatures, it contains crystals of a paraffin, heptacosane, m. p. 53—54°. P. H.

Essential Oils. SCHIMMEL & Co. (*Chem. Centr.*, 1906, ii, 1496—1498; from *Geschäftsber.*, Oct. 1906. Compare Abstr., 1906, i, 524).—The dried umbel of the bear's wort from which the fruits have been removed yields 0·08% of a brownish-yellow oil having an odour distinct from that of the fruits; it has D^{15} 0·9273, $\alpha_D - 0°48'$, acid number 16·2, ester number 148·6 before acetylation and 195·9 after. The fruits yield 0·9 to 1·21% of an oil having D^{15} 0·8744—0·8798, $\alpha_D + 0°38' — + 1°6'$, acid number 15·9—7·3, ester number 215·4—242·4 or 285·3—276·3 after acetylation. The dried ripe fruits of *Heracleum giganteum* give 3·6% of a colourless oil with a peculiar odour resembling that of the oil from ordinary bear's wort; it has D^{15} 0·8722, $\alpha_D + 1°14'$, acid number 1·6, ester number 288·3 or 314·2 after acetylation. *Basilicum* oil distilled in Germany had D^{15} 0·9038, $\alpha_D - 9°15'$, n_D^{20} 1·48132, acid number 21, ester number 11·6; on dissolving in 80% alcohol it deposited small crystals of paraffin. A sample of oil of *Calamintha Nepeta*, having D^{15} 0·9271, $\alpha_D + 6°49'$, ester number 13, contained both pulegone and methone, from which it appears probable that the ketone, calaminthone, described by Genvresse and Chablay, is not a simple substance. The oil from the blossoms of *Champaca* has D^{15} 0·8861, $\alpha_D - 11°10'$, acid number 10, ester number 21·6, or 150·1 after acetylation; it has a faint blue fluorescence in alcoholic solution, and therefore appears to contain methyl anthranilate as well as linalool. Oil of Seville oranges should have the following physical properties: D^{15} 0·854—0·857, $\alpha_D^{20} + 90 — + 93°$; α_D of the first 10% of the distillate should be higher than that of the original oil; residue 3—5%. Sweet orange oil should have D^{15} 0·848—0·853, $\alpha_D^{20} + 95—98°$; α_D of the first 10% of distillate should be only very slightly lower than that of the original oil; 2—4% residue. The oil distilled from Algerian *Pinus halepensis* is colourless, D^{15} 0·8643, $\alpha_D - 3°22'$, acid number 1·3, ester number 21·2 corresponding with 7·4 of bornyl acetate. A yield of rather less than 1% of camphor oil was obtained from the leaves or branches of camphor trees growing in German East Africa; the oil deposits camphor at the ordinary temperature; the filtrate from this camphor is a golden-yellow oil which has D^{15} 0·9236, $\alpha_D + 39°20'$; its odour is different from that of ordinary camphor oil and it solidifies on freezing; it contains 75% of camphor, traces of a phenolic substance smelling of carvacrol and still smaller quantities of borneol, but no eugenol or safrole such as are found in Japanese camphor oil. From the dried fruits of *Pastinaca sativa* 1·47% of a light yellow oil was obtained, D^{15} 0·8736, $\alpha_D - 0°9'$, n_D^{20} 1·43007, acid number 4·4, ester number 240·6, or 276 after acetylation; the dried umbels of the same plant gave 0·3% of a dark brown oil with an odour faintly resembling that of musk seed oil, D^{15} 1·0168, $\alpha_D - 0°50'$, n_D^{20} 1·50049, acid number 4·2, and ester number 62·9, or after acetylation 86·2; it dissolves in 80% alcohol and deposits paraffin; the dried roots yielded 0·35% of a light yellow oil with an odour resembling that of vetiver oil, D^{15} 1·0765, $a_D - 0°10'$, n_D^{20} 1·52502, acid number 3·9, ester number 12·6 and 33·7 after acetylation. "Essence d'avocatier" obtained from *Persea gratissima* is a light yellowish-green oil having a bitter taste and an odour resembling that of aniseed, D^{15} 0·956, $a_D + 2°22'$, n_D^{20} 1·51389, ester number 3·8 or after acetylation 18·9; it consists chiefly of methylchavicol, *a*-pinene, and a paraffin of m. p. 53—54°. The turpentine, obtained from *Pinus Sabiniana*, which contains abietene, yielded on steam distillation 8·44% of a clear, colourless oil, D^{15} 0·6962, $a_D - 0°9'$; the chief fraction obtained from this, which boiled at 98·5—99°, was optically inactive, had D^{15} 0·6880, and was identical with *n*-heptane, described by Thorpe as being obtained from the same source. A Spanish hop oil obtained from *Origanum Smyrnaeum* was found to contain cedar camphor; this is, however, not a normal constituent, and may have been introduced by adulteration with cedar oil.

The following oils are described for the first time. A yellowish-green, mobile oil obtained from *Evodia simplex*; it has a pleasant smell, D^{15} 0·9737, $a_D - 13°4'$, acid number 2·1, ester number 16·4 or after acetylation 63·3; it contains methoxyeugenol and a paraffin of m. p. 80—81°. Pilea oil obtained from *Pilea*, species not stated, is a very limpid, clear oil smelling of turpentine; it has D^{15} 0·8533, $a_D + 33°53'$, n_D^{20} 1·46862, ester number 5·1 or after acetylation 24·2; it contains pinene, but the chief constituent was not identified. Oil of white dittany from Algiers, probably obtained from *Amaricus Dictamnus* (*Origanum Dictamnus*), has a yellow colour; it contains 85% of pulegone, of which it smells strongly, and has D^{15} 0·9331 and $a_D + 3°$.

As phenylcarbimide is not always suitable for identifying alcohols, the authors have experimented with *a*-naphthylcarbimide, and have prepared the following carbamates. *Geranyl a-naphthylcarbamate*, prisms from dilute methyl alcohol, m. p. 47—48°. *Dihydrocuminyl a-naphthylcarbamate*, prisms from methyl alcohol, m. p. 146—147° (?). The *a-naphthylcarbamate* obtained from terpineol (m. p. 35°) separates from dilute alcohol in feathery prisms, m. p. 147—148°; the corresponding derivative obtained from terpineol (m. p. 32°) separates from alcohol in prisms, m. p. 83—84°. *Linalyl a-naphthylcarbamate*, needles from dilute alcohol, m. p. 53°. Nerol and citronellol give only oily naphthylcarbamates, which could not be made to crystallise.

P. H.

American Copals. CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1906, [iii], 35, 1143—1150).—Demerara copal has D^{19} 1·047, m. p. 180, acid number 97·7, and Köttsdorfer number 102·4.

Columbian copal has D^{19} 1·054, m. p. $> 300°$, acid number 118·8, and Köttsdorfer number 155·7.

Brazilian copal has D^{19} 1·053, m. p. 100°, acid number 123, and Köttsdorfer number 133·3.

The solubilities of these three copals in twelve organic solvents are tabulated in the original, which also gives descriptions of the three resins.

T. A. H.

Vicianin, a new Cyanogenetic Glucoside contained in the Seeds of Vetch. GABRIEL BERTRAND (*Compt. rend.*, 1906, **143** 832—834).—The cyanogenetic principle observed in the seeds of *Vicia angustifolia* by Bruyning and Van Haarst (Abstr., 1900, ii, 160) is a glucoside *vicianin* which is present to the extent of 0·9°/$_0$, and can be obtained in a crystalline form by extracting the powdered seeds with alcohol at the ordinary temperature, evaporating the solution in a vacuum, extracting the residual syrup several times with ether, and finally filtering the insoluble residue and washing with cold water, then with alcohol. *Vicianin* crystallises from hot water in tufts of brilliant, colourless needles, m. p. 160°, $[\alpha]_D^{16-19^\circ} -20·7°$ in saturated aqueous solution; it contains 3·2°/$_0$ of nitrogen which is liberated in the form of hydrogen cyanide by the action of emulsin. The seeds of *Vicia angustifolia*, which are capable of furnishing 0·75 gram hydrogen cyanide per kilo., are not a suitable food-stuff for domestic animals.

M. A. W.

Crystalline Substances of Prickly Ash Bark. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1906, **28**, 1649—1657).—The isolation of a crystalline substance "xanthoxylin" from the bark of the northern prickly ash (*Xanthoxylum fraxineum* syn. *X. Americanum*) was first accomplished by Staples (*Amer. J. Pharm.*, 1829, 163), and later by Lloyd (*Amer. J. Pharm.*, 1890, 229) and Eberhardt (*Amer. J. Pharm.*, 1890, 231). Another crystalline substance was obtained by Colton (*Amer. J. Pharm.*, 1890, 191) from the southern prickly ash (*X. Carolinianum* syn. *X. Clava-Herculis*), but was shown by Eberhardt (*loc. cit.*) to differ from that yielded by *X. fraxineum*. A third "xanthoxylin" was extracted by Stenhouse from *X. piperatum* (*Annalen*, 1854, **89**, 257; 1857, **104**, 236), which is quite different from the two former substances, and is isomeric with cantharidin. It is now proposed to retain the name "xanthoxylin" for the last-mentioned substance, and to designate the products of the northern and southern prickly ash as "xanthoxylin N" and "xanthoxylin S" respectively.

Xanthoxylin N, $C_{14}H_{11}O_3(OMe)$, m. p. 132·5°, crystallises in white needles, is optically inactive, and gives a red coloration with sulphuric acid. The *dibromide*, $C_{15}H_{14}O_4Br_2,H_2O$, m. p. 171°, crystallises in white aggregates, and becomes yellow on prolonged exposure to the light. On reducing xanthoxylin N with hydrogen iodide, *dihydroxanthoxylin N*, $C_{15}H_{16}O_4$, m. p. 142—143°, is obtained, which forms white needles. Xanthoxylin N does not yield a benzoyl derivative or an anilide. When the substance is dissolved in excess of potassium hydroxide and titrated with acid, it does not exhibit acid properties with methyl-orange, but acts with phenolphthalein as a monobasic acid. With resorcinol it behaves like the anhydride of a dibasic acid and gives a brilliant phthalein reaction.

Xanthoxylin S, $C_{14}H_{12}O_4$, m. p. 119—120°, forms snow-white crystals, does not contain a methoxyl group, and is possibly an alcohol or phenol of which xanthoxylin N is the methyl ether.

E. G.

Chlorophyll. I. Separation and Characterisation of Chlorophyll Derivatives. RICHARD WILLSTÄTTER and WALTER MIEG (*Annalen*, 1906, 350, 1—47).—Of the products obtained chiefly by Schunck and Marchlewski from chlorophyll by the regulated action of acids and alkalis, only phylloporphyrin has been purified with certainty by means of its sparingly soluble zinc salt; alkachlorophyll, phylloxanthin, phyllocyanin, and phyllotaonin, have not been obtained pure, and it is doubtful whether they are all individual substances. The authors have submitted extracts of chlorophyll to the action of acids and alkalis, and have obtained mixtures of substances which can be separated by means of their varying acidity. These substances are arranged into two classes: (1) *phytochlorins*, which dissolve in neutral solvents to olive-green or green solutions, and in acid solvents to blue or greenish-blue solutions; (2) *phytorhodins*, which form blue or green solutions in acid, and red solutions in neutral, solvents. The various members are denoted by the letters *a*, *b*, *c*, &c.

Phytochlorins and phytorhodins are insoluble in water, but dissolve in organic solvents, alkali and ammonium hydroxides, and sodium hydrogen carbonate; they do not contain phenolic hydroxyl, but an acid group is present, in virtue of which esters can be obtained; they are weak bases forming salts which are decomposed by water.

To obtain the chlorophyll extracts, the dried leaves of the stinging-nettle are treated with light petroleum to remove yellow pigments, and are then either boiled with alcohol or ethyl acetate, or extracted with cold alcohol.

To obtain phytochlorin *a* and *b*, and phytorhodin *f*, the extract obtained by the first method is dissolved in 96% alcohol, sufficient alcoholic potash added to make a 2% solution, and the mixture boiled for fifteen minutes. After diluting with water and neutralising, the solution is extracted with ether; from the ethereal solution after special treatment, alcoholic hydrogen chloride of 3% strength extracts phytochlorin *b*, of 6% strength extracts phytochlorin *a*, and of 11% strength extracts phytorhodin *f*.

Phytochlorin *c* and *d* are obtained by treating *a* or *b* with concentrated alcoholic hydrogen chloride in darkness for twenty-five days; *c* and *d* are extracted from ether by 0·5% and 1·5% alcoholic hydrogen chloride respectively.

To obtain phytorhodins, the cold alcoholic extract of the dried leaves is treated with potassium hydroxide, whereby a greenish-black salt of an alkachlorophyll is precipitated; alcoholic calcium chloride causes the separation of a calcium compound of the substance still remaining in the mother liquor. The finely-powdered potassium salt or the calcium compound is heated with 20% alcoholic hydrogen chloride for seven hours; from the reaction products phytorhodin *a* and its ethyl ester, phytorhodin *b* and its ester, and phytorhodins *c*, *d*, and *e* are ultimately isolated.

Phytochlorin a, $C_{28}H_{33}O_5N_3$, is obtained by the slow evaporation of its benzene or alcoholic solution in characteristic rosettes of slender blue-black needles, olive-brown by transmitted light, m. p. 181—182°, decomposing. By repeated crystallisation or by heating in a toluene bath, it appears to lose $\frac{1}{2}H_2O$, becomes insoluble in ether, and then has

m. p. >200°. Very characteristic of phytochlorin *a* is the splendid blue colour of its solution in glacial acetic acid. The substance has weak basic and pronounced acid properties, and is readily attacked by oxidising or reducing agents.

Phytochlorin b, $C_{28}H_{33}O_5N_3$, separates from alcohol and benzene in a blue-black, metallic-looking, crystalline mass of prisms and plates, sinters at 168°, m. p. 183—190°, decomposing. It dissolves in alkalis, forms a copper salt, and is a stronger base than phytochlorin *a*. Assuming the substance to be a monobasic acid, the analysis of the cæsium salt indicates a molecular weight of 488. By heating for one to two hours with methyl alcoholic hydrogen chloride, phytochlorin *b* is converted partially into a *substance*, $C_{58}H_{68}O_9N_6$, devoid of acid character, which separates from methyl alcohol in aggregates of steel-blue, rectangular plates and prisms, m. p. 140°, yields phytochlorin *b* by hydrolysis, and seems to be the methyl ester resulting from 2 mols. of the latter by loss of 1 mol. H_2O.

Phytochlorin *a* is converted into *b* by concentrated alcoholic alkali hydroxide.

Phytochlorin c, $C_{28}H_{33}O_6N_3$, forms by slow separation from methyl alcohol elongated crystals, which acquire an S shape by rapid separation. It differs from phytochlorin a and b in its more pronounced basic character and in the colour of its solutions.

Phytochlorin d, $C_{28}H_{35}O_6N_3$, is the strongest base of the series, and is characterised by the magnificent colour of its solutions; the aqueous solution is violet with a strong red fluorescence. The sodium salt is dissociated hydrolytically in dilute solution. From ether, the substance separates in tufts of needles, and in twinned, truncated prisms from alcohol; although comparatively stable towards reagents, it readily loses water, forming a mixture of weaker bases. When strongly heated, it evolves a vapour having the odour of tobacco and giving the pyrrole test with a pine shaving.

Phytorhodin a, $C_{28}H_{35}O_6N_3$, is obtained in tufts of needles by the slow evaporation of its ethereal solution. It is blue-black by reflected, reddish-brown by transmitted, light, has m. p. 130—140°, and dissolves in dilute alkalis or acids. The *ethyl* ester, $C_{30}H_{37}O_5N_3$, forms microscopic prisms, is insoluble in alkalis, melts indefinitely below 100°, decomposes at higher temperatures, and yields phytorhodin a by hydrolysis. The ester is formed with elimination of H_2O.

Phytorhodin b, $C_{28}H_{33}O_4N_3$, forms rhombic plates which are frequently twinned and appear reddish-brown by transmitted light, decomposes by heating, and forms solutions with characteristic colours. Sodium hydroxide (0·01% solution) precipitates an acid sodium salt from the ethereal solution, whereas stronger solutions of the alkali (0·1 to 1%) form a soluble salt, which, however, is precipitated by an 8% solution. The *ethyl* ester, $C_{30}H_{37}O_4N_3$, crystallises well from benzene or ether in plates, m. p. 76—80°, decomposing, yields phytorhodin b by hydrolysis with 13% hydrogen chloride, a more basic substance with concentrated hydrogen chloride, and a substance similar to, but less basic than, phytorhodin a with boiling alcoholic potash. The ester is decomposed by heating, forming a vapour which distinctly reddens shavings moistened with hydrochloric acid.

Phytorhodin c, $C_{56}H_{68}O_9N_6$, separates from ether in tufts of slender needles and dissolves in 1°/$_0$ sodium hydroxide solution.

Phytorhodin d, $C_{56}H_{60}O_{11}N_6$, and *phytorhodin e*, $C_{28}H_{31}O_4N_3$, resemble one another closely, but differ in the colour of their solutions. Both are separated from chloroform solution by ether in radiating groups of prisms.

Phytorhodin f, $C_{26}H_{29}O_5N_3$, $C_{28}H_{29}O_6N_2$ or $C_{26}H_{29}O_5N_3,1{\cdot}5H_2O$, forms rosettes of black prisms, is sparingly soluble in ether, and exhibits great stability, not being affected by a short boiling with methyl alcoholic potash.

When alcoholic solutions of phytochlorins or of phytorhodins are treated with alcoholic zinc or copper acetates, intensely coloured complex double salts are obtained, which are insoluble in ether, but by treatment with excess of hydrochloric or acetic acid are rendered soluble. The compounds (but not those of the esters) are soluble in alkali hydroxides; the zinc salts are decomposed by 10—20°/$_0$ alcoholic hydrogen chloride, whereas the copper compounds dissolve unchanged in the concentrated acid. C. S.

Composition of Chlorophyll. Richard Willstätter (*Annalen*, 1906, **350**, 48—82).—The author criticises adversely Stoklasa's "lecithin" theory of the constitution of chlorophyll (compare Abstr., 1896, ii, 266; 1897, ii, 116), since chlorophyll from fresh stinging nettle or grass contains only 0·0108°/$_0$ and 0·0746°/$_0$ of phosphorus respectively, and that from the dried nettle, purified by the colloidal process, does not contain any.

The crude chlorophyll extracted by methyl or ethyl alcohol or acetone from dried nettle leaves is to some extent purified by two methods: (1) Kraus's method (compare Sorby, *Proc. Roy. Soc.*, 1873, **21**, 442), in which the author uses methyl alcohol and gasoline in the place of ethyl alcohol and benzene respectively; (2) the colloidal process, in which an alcoholic or acetone solution of chlorophyll is diluted with 3 vols. of water and treated with ether, which extracts carotin and other impurities; the aqueous-alcoholic or aqueous-acetone solution is now treated with calcium chloride, after which ether extracts the chlorophyll from the solution. The purified chlorophyll is a dark green substance of the consistency of wax, which dissolves in neutral solvents, forming solutions with a brilliant bluish-green colour and pronounced red fluorescence.

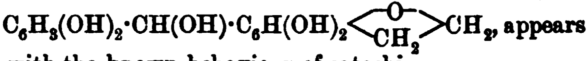
The ash of chlorophyll purified by the first process is 1·84°/$_0$, containing 1·67°/$_0$ of magnesium oxide; chlorophyll purified by the colloidal process leaves 3·14—3·36°/$_0$ of ash containing 1·51—1·71°/$_0$ of magnesium oxide; in neither case is iron present. Nitric acid of D 1·4 converts chlorophyll into a colourless oil.

As an ester, chlorophyll is hydrolysed by alkalis, yielding an *alcohol* having the approximate composition $C_{20}H_{40}O$ and *chlorophyllin*, a complex substance of acid character, containing magnesium, stable to alkalis, but decomposed by acids.

Chlorophyllin is obtained by treating the alcoholic extract of the nettle or of grass with cold methyl alcoholic potash for twenty-four hours, diluting the solution with water to dissolve the precipitated potassium salt, adding ether to extract impurities, acidifying most carefully with phosphoric acid and finally with monosodium phosphate, and extracting the chlorophyllin with ether. Two methods of purification are adopted. In virtue of its acid character chlorophyllin is separated from weaker acid and from neutral impurities by extracting the ethereal solution with sodium hydrogen carbonate or disodium phosphate, the chlorophyllin in the latter case being liberated again by the addition of monosodium phosphate. Chlorophyllin, the yield of which is 0·15% of the weight of leaf extracted, is a glistening, metallic-looking substance which contains 3·54% of magnesium oxide, and forms an intensely bluish-green ethereal solution with a strong red fluorescence which disappears by dilution; chlorophyllin prepared at higher temperatures exhibits fluorescence in extremely dilute solution. Chlorophyllin is decolorised by nitric acid of D 1·4 without the separation of an oil, whilst concentrated alcoholic hydrogen chloride changes it into an unstable basic substance (compare preceding abstract). The *barium* and *potassium* salts are precipitated by treating the ethereal solution with the corresponding hydroxides. The alkali salts of chlorophyllin prepared in the cold dissolve in water, forming green solutions without fluorescence, whereas the potassium salt of chlorophyllin prepared by boiling alcoholic potash forms a violet or red fluorescent aqueous solution, somewhat resembling that of alkachorophyll; the author regards the last-mentioned substance as a mixture of the chlorophyllins obtained by the action of cold and of boiling alkali on chlorophyll. C. S.

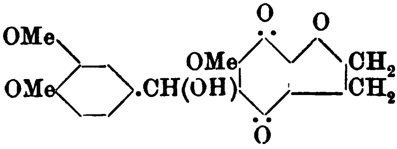
Filicitannic Acid. W. WOLLENWEBER (*Arch. Pharm.*, 1906, **244**, 466—486. Compare Reich, Abstr., 1901, i, 212).—By extracting the powdered *Filix* rhizomes with absolute alcohol, distilling off the alcohol under diminished pressure, and shaking the residue with ether, the filicitannic acid is obtained as an insoluble residue in yield of 7·8%. This is the natural, or *proto-*, *filicitannic acid*; it has the composition $C_{41}H_{44}O_{24}N,2H_2O$, is very soluble in water, yielding a solution that lathers, has an astringent taste, tans leather, precipitates gelatin and albumin, reduces ammoniacal silver and alkaline copper solutions, gives a transient green coloration with ferric chloride, and reddens a deal splint that has been moistened with hydrochloric acid. At 100° it loses $2H_2O$; the residue is still soluble in water. When heated at 125°, or when it is precipitated with lead acetate and the precipitate is decomposed with hydrogen sulphide, it is converted into *filicitannic anhydride*, $C_{41}H_{36}O_{18}N$, which is insoluble in water. At 148° this yields a *second anhydride*, $C_{41}H_{32}O_{16}N$.

The acid has a molecular weight of about 470 (determined cryoscopically in aqueous solution), corresponding with half the formula given above, and it diffuses through parchment-paper much more rapidly than tannin, but yet as a single substance, the percentage of nitrogen being the same in the portion which has diffused as in that which has not yet diffused. The barium salt, $(C_{41}H_{33}O_{18}N)_2Ba_3$, obtained as a reddish-brown, amorphous precipitate when barium chloride is added to an aqueous solution of the acid mixed with ammonia, is derived from the anhydride. The bromine derivative, $C_{41}H_{40}O_{24}NBr_8$, obtained by the action of bromine on a concentrated aqueous solution of the acid, is identical with that obtained by the action of bromine on a solution of the acid in dilute aqueous potassium hydroxide. When the acid is mixed with soda-lime and zinc dust and heated in a current of hydrogen gas, the distillate obtained resembles impure pyrrole. C. F. B.

Catechin. Stanislaus von Kostanecki and Victor Lampe (*Ber.*, 1906, **39**, 4007—4014. Compare Abstr., 1902, i, 553, 637; A. G. Perkin, Trans., 1902, **81**, 1160).—The authors are of the opinion that catechin contains a coumaran and not a chroman group and that the six-carbon ring has one unsubstituted hydrogen, since a monobromo-derivative only can be obtained. The catechol residue is therefore presumably attached to the benzene and not to the furan ring of the coumaran radicle by means of a secondary alcoholic group. The formula,  $C_6H_3(OH)_2\cdot CH(OH)\cdot C_6H(OH)_2{<}\begin{smallmatrix}O\\ CH_2\end{smallmatrix}{>}CH_2$, appears to be in harmony with the known behaviour of catechin.

Pentamethyl catechin, $C_{15}H_9O(OMe)_5$, is formed as a by-product in the preparation of the tetramethyl ether and is readily prepared by the action of a large excess of methyl sulphate on the latter. It crystallises from alcohol in colourless needles, m. p. 95°, and cannot be acetylated. Monobromocatechin tetramethyl ether (Abstr., 1902, i, 637) crystallises in colourless needles, m. p. 173—174°, and is most readily obtained by bromination in sunlight. When oxidised with permanganate, it yields veratric acid and hence probably contains the bromine atom in the six-membered carbon ring of the coumaran molecule; it cannot be oxidised by chromic acid to a catechone derivative. The pentamethyl ether yields a *bromo*-derivative, $C_{15}H_8OBr(OMe)_5$, m. p. 142—144°.

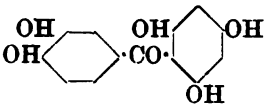
Catechone trimethyl ether, when oxidised with cold permanganate, yields veratric acid and hence probably has the constitution



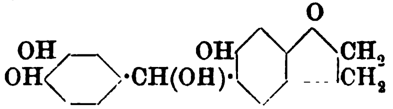
Catechone tetramethyl ether, $C_{19}H_{20}O_7$, obtained by oxidising catechin pentamethyl ether with an acetic acid solution of chromic acid, crystallises from alcohol in yellow needles, m. p. 174—175°.

Nitrotrimethylcatechone (Karnowski and Tambor, Abstr., 1902, i, 637), when oxidised with cold permanganate, yields Tiemann and Matsmoto's 6-nitroveratric acid (compare Zincke, Abstr., 1897, i, 59). J. J. S.

Maclurin. Stanislaus von Kostanecki and Victor Lampe (*Ber.*, 1906, **39**, 4014—4021. Compare Ciamician and Silber, Abstr., 1894, i, 471; 1895, i, 538; König and Kostanecki, *ibid.*, 1894, i, 534; Komarowsky and Kostanecki, *ibid.*, 1894, i, 506.)—If catechin has the constitution assigned to it in the preceding abstract, it is the coumaran derivative of leucomaclurin;



Maclurin.



Catechin.

Maclurin pentamethyl ether, 2 : 4 : 6 : 3′ : 4′-pentamethoxybenzophenone (W. H. Perkin, junr., and Robinson, Proc., 1906, **22**, 305), may be obtained by methylating maclurin with hot concentrated potassium hydroxide solution and an excess of methyl sulphate. It is identical with Ciamician and Silber's veratroylphloroglucinol trimethyl ether (Abstr., 1892, 873). When reduced with alcoholic potash and zinc dust, the ether yields *leucomaclurin pentamethyl ether* (*2 : 4 : 6 : 3′ : 4′-pentamethoxybenzhydrol*), $C_6H_3(OMe)_2{\cdot}CH(OH){\cdot}C_6H_2(OMe)_3$, which crystallises from alcohol in brilliant, prismatic needles, m. p. 109—110°. It dissolves in concentrated sulphuric acid to a red solution, and when oxidised with chromic acid yields 2 : 6-dimethoxybenzoquinone and veratric acid.

2 : 4 : 6-*Trimethoxybenzhydrol* (*leucobenzophloroglucinol trimethyl ether*), $OH{\cdot}CHPh{\cdot}C_6H_2(OMe)_3$, obtained by reducing benzophloroglucinol trimethyl ether, crystallises in large prisms, m. p. 124—126°, and when oxidised yields 2 : 6-dimethoxybenzoquinone together with benzaldehyde and benzoic acid.

Benzhydrol ethers are readily obtained by boiling solutions of benzhydrol in various alcohols with hydrochloric acid. The *methyl ether*, $CHPh_2{\cdot}OMe$, has b. p. 270—271°, the *ethyl ether* 288°.

Attempts to methylate leucobenzophloroglucinol trimethyl ether give rise to *benzylidenediphloroglucinol hexamethyl ether*,

$$CHPh[C_6H_2(OMe)_3]_2,$$

which crystallises in colourless prisms, m. p. 181—182°. The same compound is readily synthesised by condensing benzaldehyde with trimethylphloroglucinol and when oxidised yields dimethoxybenzoquinone, benzaldehyde, and benzoic acid.

3 : 4-*Dimethoxybenzylidenediphloroglucinol hexamethyl ether*,

$$C_6H_3(OMe)_2{\cdot}CH[C_6H_2(OMe)_3]_2,$$

obtained by boiling an alcoholic solution of leucopentamethylmaclurin with a few drops of hydrochloric acid, crystallises in colourless prisms, m. p. 145—146°.

2 : 4 : 6-*Trimethoxybenzhydrol methyl ether*,

$$C_6H_5{\cdot}CH(OMe){\cdot}C_6H_2(OMe)_3,$$

may be prepared by heating trimethoxybenzhydrol with acetic anhydride and sodium acetate and crystallising the product from methyl alcohol, it forms colourless prisms, m. p. 79—80°; the corresponding *ethyl ether*, $C_6H_5{\cdot}CH(OEt){\cdot}C_6H_2(OMe)_3$, m. p. 72—73°.

2 : 4 : 6 : 3′ : 4′-*Pentamethoxybenzhydrol methyl ether*,

$$C_6H_3(OMe)_2{\cdot}CH(OMe){\cdot}C_6H_2(OMe)_3,$$

m. p. 94—96°. When oxidised, these ethers yield the same products as the methoxybenzhydrols themselves. Many of the compounds give characteristic purple colorations when the solutions containing hydrochloric acid are exposed to sunlight. J. J. S.

Synthesis of Maclurin Pentamethyl Ether. STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1906, **39**, 4022—4027).—Maclurin pentamethyl ether (2:4:6:3′:4′-pentamethoxybenzophenone; preceding abstract), has been synthesised by a method identical with that used by W. H. Perkin, junr., and Robinson (Proc., 1906, **22**, 305).

2 : 4 : 6 : 4′-*Tetramethoxybenzophenone*, $C_{17}H_{18}O_5$, obtained by Friedel-Craft's synthesis from anisoyl chloride and phloroglucinol trimethyl, crystallises from alcohol in short, colourless prisms, m. p. 146°. The ether corresponding *leuco*-compound, $C_6H_2(OMe)_3\cdot CH(OH)\cdot C_6H_4\cdot OMe$, m. p. 103°; its concentrated sulphuric acid solution has an orange-yellow colour, and its alcoholic solution yields a purple colour with hydrochloric acid when exposed to sunlight.

2 : 4 : 6 : 3′ : 4′ : 5′-*Hexamethoxybenzophenone*, $C_{19}H_{22}O_7$, m. p. 122°, is obtained from trimethylgalloyl chloride and phloroglucinoltrimethyl ether; its *leuco*-compound, $C_{19}H_{24}O_7$, has m. p. 124—125°.

3 : 4 : 3′ : 4′ : 5′-*Pentamethoxybenzophenone*,

$$C_6H_3(OMe)_2\cdot CO\cdot C_6H_2(OMe)_3,$$

obtained from trimethylgalloyl chloride and veratrole, has m. p. 118°. Anisoyl chloride and veratrole yield 3 : 4 : 4′-*trimethoxybenzophenone*, $C_{16}H_{16}O_4$, m. p. 98—99°; the same compound may be obtained by condensing veratroyl chloride with anisole, whence its constitution.

3 : 4 : 3′ : 4′-*Tetramethoxybenzophenone*, $C_{17}H_{18}O_5$, m. p. 145°, is obtained from veratroyl chloride and veratrole. J. J. S.

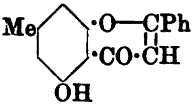
***o*-Hydroxyfurfurylidene-acetophenones.** ST. COURANT and STANISLAUS VON KOSTANECKI (*Ber.*, 1906, **39**, 4031—4034).—*o*-Hydroxychalkones, when boiled with mineral acids, are readily converted into flavanones; the corresponding *o*-hydroxyfurfurylidene-acetophenones, when boiled with mineral acids, combine with water (2 mol.), yielding hydroxyphenacyl-lævulic acids (Marckwald, Abstr., 1888, 135, 677; Kehrer, 1901, i, 389). *Furfurylidenepaeonol*, $OH\cdot C_6H_3(OMe)\cdot CO\cdot CH{:}CH\cdot C_4OH_3$ [CO:OH:OMe = 1 : 2 : 4], obtained by the condensation of paeonol with furfuraldehyde in the presence of alcohol and 50% sodium hydroxide solution, crystallises from alcohol in long, yellow needles, m. p. 112°; it yields a sparingly soluble *sodium* salt, and when boiled with aqueous alcoholic hydrochloric acid yields 2-*hydroxy*-4-*methoxyphenacyl*-*lævulic acid*,

$$OH\cdot C_6H_3(OMe)\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H,$$

which crystallises from dilute alcohol in long, colourless needles, m. p. 165—166°.

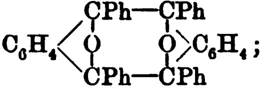
Furfurylidene-2-*hydroxy*-5-*methoxyacetophenone* forms orange-red needles, m. p. 75°, and yields 2-*hydroxy*-5-*methoxyphenacyl*-*lævulic acid*, m. p. 125°. J. J. S.

Synthesis of 1-Hydroxy-3-methylflavone. S. LUDWINOWSKY and JOSEF TAMBOR (*Ber.*, 1906, **39**, 4037—4041).—Rasinski's orcacetophenone is shown to be 1 : 6-dihydroxy-4-methylacetophenone. The *dimethyl ether*, $C_6H_2Me(OMe)_2\cdot COMe$, may be prepared by Friedel-Craft's synthesis from orcinol dimethyl ether; it crystallises from dilute alcohol in colourless prisms, m. p. 89°, b. p. 222°/720 mm., and condenses with ethyl benzoate in the presence of sodium, yielding 2 : 6-*dimethoxy*-4-*methylbenzoylacetophenone*, $C_6H_2Me(OMe)_2\cdot CO\cdot CH_2\cdot COPh$, which crystallises from concentrated alcohol in tabular prisms, m. p. 98—99°. When boiled with hydriodic acid, D 2·0, the ketone yields 1-*hydroxy-3-methylflavone*, in the form of yellow, lustrous needles, m. p. 143°. It forms a sparingly soluble *sodium* salt and is thus shown to be a 1-hydroxyflavone. The *acetyl* derivative, $C_{15}H_8MeO_2 \cdot OAc$, m. p. 132°. J. J. S.



Derivative of Dihydro*iso*benzofuran. Part IV.

ALFRED GUYOT and J. CATEL (*Bull. Soc. chim.*, 1906, [iii], **35**, 1124—1135. Compare Abstr., 1906, i, 761).—Most of the facts recorded in this paper have already been given in Abstr., 1905, i, 540. *o*-Benzhydryltriphenylcarbinol is formed when phenylphthalide reacts with an excess of magnesium phenyl bromide in ether, but if the phenylphthalide is in excess the principal product is 2-hydroxy-1 : 2-diphenyl-1 : 2-dihydro*iso*benzofuran, $C_6H_4 < \begin{matrix} CHPh \\ CPh(OH) \end{matrix} > O$.

The product formed by the dehydration of the latter is now shown to be 1 : 2-diphenyl*iso*benzofuran, $C_6H_4 \lessdot \begin{matrix} CPh \\ CPh \end{matrix} > O$, which on solution in benzene or alcohol and exposure to light in the absence of air polymerises, forming a *substance*, ; this occurs in small, faintly yellow crystals, is scarcely soluble in organic solvents, and when heated regenerates 1 : 2-diphenyl*iso*benzofuran.

Similar solutions of the latter on exposure to air in the dark furnish *o*-dibenzoylbenzene, and the same transformation takes place when the solutions are exposed to the joint action of air and light.

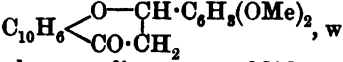
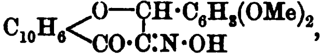
o-Dibenzhydrylbenzene, $C_6H_4(CHPh \cdot OH)_2$, produced by reducing 2-hydroxy-1 : 2-diphenyl-1 : 2-dihydro*iso*benzofuran or *o*-dibenzoylbenzene with sodium amalgam, forms small, faintly yellow crystals, and when dehydrated by sulphuric acid (Abstr., 1906, i, 761) furnishes phenylanthracene.

When hydrochloric acid is used as the dehydrating agent, 1 : 2-diphenyl-1 : 2-dihydro*iso*benzofuran is produced, which forms small, faintly yellow crystals, m. p. 95°, is soluble in most organic solvents and, on treatment with sulphuric acid, is converted into phenylanthracene. T. A. H.

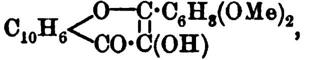
3′ : 4′-Dihydroxy-α-naphthaflavonol.

P. BIGLER and STANISLAUS VON KOSTANECKI (*Ber.*, 1906, **39**, 4034—4037).—*3′ : 4′-Dimethoxybenzylidene-2-acetyl-1-naphthol*,

$$C_6H_4 < \begin{matrix} C(OH) \\ CH \colon CH \end{matrix} > C \cdot CO \cdot CH \colon CH \cdot C_6H_3(OMe)_2,$$

obtained by the condensation of veratraldehyde with 2-acetyl-1-naphthol in the presence of aqueous alcoholic sodium hydroxide, crystallises in red prisms with a violet lustre, m. p. 134·5°. Its solution in concentrated sulphuric acid has a violet-red colour. The *acetyl* derivative, $OAc \cdot C_{10}H_6 \cdot CO \cdot CH \colon CH \cdot C_6H_3(OMe)_2$, crystallises from alcohol in yellow plates, m. p. 139·5°. When boiled with aqueous alcoholic hydrochloric acid, the naphthol derivative yields 3′:4′-*dimethoxy-a-naphthaflavanone*,  $C_{10}H_6<\begin{matrix}O-CH\cdot C_6H_3(OMe)_2\\ CO\cdot CH_2\end{matrix}$, which crystallises from alcohol in colourless needles, m. p. 135°, and is soluble in concentrated sulphuric acid to an orange-coloured solution. The *isonitroso*-derivative,  $C_{10}H_6<\begin{matrix}O-CH\cdot C_6H_3(OMe)_2\\ CO\cdot C{:}N\cdot OH\end{matrix}$, forms long, yellow needles melting and decomposing at 156°. It dissolves in dilute sodium hydroxide solution, dyes orange with cobalt mordants, but yellow with uranium, cadmium, and lead mordants.

When an acetic acid solution of the *iso*nitroso-compound is boiled with 10°/₀ sulphuric acid, 3′ : 4′-*dimethoxy-a-naphthaflavonol*,



$$C_{10}H_6<\begin{matrix}O-C\cdot C_6H_3(OMe)_2\\ CO\cdot C(OH)\end{matrix},$$

is formed. It crystallises from alcohol in yellow needles, m. p. 224°, and dissolves in concentrated sulphuric acid to a yellow solution with a green fluorescence. The *sodium* salt is sparingly soluble and the *acetyl* derivative is colourless, m. p. 191—192°.

3′ : 4′-*Dihydroxy-a-naphthaflavonol*, m. p. 286°, forms yellow, glistening needles containing water of crystallisation. It becomes opaque on exposure to the air. The *triacetyl* derivative forms needles, m. p. 215°. J. J. S.

Optical Isomerides of Arginine and Ornithine. OTTO RIESSER (*Zeit. physiol. Chem.*, 1906, **49**, 210—246. Compare Kutscher, Abstr., 1901, i, 561).—Full details are given for the preparation of *d*-arginine by a modification of E. Fischer's method (*Ber.*, 1905, **38**, 4187). One of the simplest methods of purification is by means of the picrate.

d-Arginine nitrate, $C_6H_{14}O_2N_4,HNO_3,\frac{1}{2}H_2O$, has m. p. 126° (not 175° as stated by Gulewitsch, Abstr., 1899, 833), and the dinitrate, m. p. about 250° (Kanitz, *Zeit. physiol. Chem.*, 1906, **47**, 491). The picrolonate (Steudel, Abstr., 1903, i, 431), m. p. 231°, contains $1H_2O$, and its solubility in water at 16° is 0·05. The *β-naphthalene sulphone* derivative, $C_6H_{13}O_2N_4\cdot SO_2\cdot C_{10}H_7$, forms a colourless powder, m. p. 88—89°.

A 50°/₀ yield of the racemic modification of arginine may be obtained by heating *d*-arginine sulphate with 50°/₀ sulphuric acid for thirty-three hours at 160—180°; *r*-ornithine is formed at the same time. r-*Arginine carbonate* is harder and more hygroscopic than the *d*-isomeride. The r-*picrate* crystallises in anhydrous, glistening prisms, m. p. 200—201°, and its solubility in water at 16° is 0·22, whereas that of the isomeric *d*-compound in 0·5. The nitrate is sparingly soluble, m. p. 217° (not 211° as stated by Kutscher). A *dinitrate*, $C_6H_{14}O_2N_2,2HNO_3$, forms large crystals, readily soluble in water; m. p. 151°. The r-*cupric nitrate* derivative, $2C_6H_{14}O_2N_4,Cu(NO_3)_2,3H_2O$, has m. p. 228—229°. The *silver nitrate* derivative,

$$(C_6H_{14}O_2N_4,HNO_3)_2,AgNO_3,\tfrac{1}{2}H_2O,$$

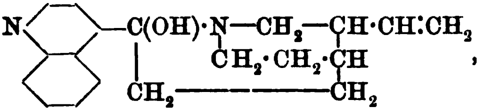
has m. p. 170—172°, and the r-*picrolonate*, m. p. 248°, is anhydrous, and its solubility in water at 16° is 0·03. The *β-naphthalene sulphone* derivative, $C_6H_{13}O_2H_4\cdot SO_2\cdot C_{10}H_7,\frac{1}{2}H_2O$, has not a sharp melting point.

l-*Arginine* may be obtained from the *r*-compound by means of arginase (Kossel and Dakin, Abstr., 1904, ii, 425), which transforms *d*-arginine into *d*-ornithine and carbamide. The picrate, nitrate, dinitrate, cupric nitrate, silver nitrate, picrolonate, and naphthalene sulphone derivative have been prepared and resemble the corresponding derivatives of the *d*-base.

β-Naphthalene sulphone-d-*ornithine*, $C_5H_{10}O_2N_2(SO_2{\cdot}C_{10}H_7)_2$, m. p. 189°, is less soluble in water or alcohol than the corresponding arginine derivative.

r-*Ornithine picrate*, $C_5H_{12}O_2N_2,2C_6H_3O_7N_3,2\frac{1}{2}H_2O$, crystallises in ochre-yellow plates, m. p. 183—184°, decomposing. *β-Naphthalene sulphone*-r-*ornithine* is anhydrous, m. p. 195—196°. J. J. S.

Cinchona Alkaloids. I. Paul Rabe (*Annalen*, 1906, **350**, 180—203. Compare Rabe and Ritter, Abstr., 1905, i, 811).—Koenigs' formula of cinchonine (Abstr., 1906, i, 762) explains the formation of cinchene by hydrolysis; the author proposes the formula, to account for the facts that cinchotoxine forms only a mono*iso*nitroso-compound, and that *iso*nitrosocinchotoxine by the Beckmann transformation yields cinchoninic acid and meroquineninenitrile.



[With Karl Ritter.]—The nitrile of *N*-methylmeroquinenine has b. p. 162°/49 mm., 252—255°/741 mm., D_4^{20} 0·9505, n_D^{20} 1·4803, $[\alpha]_D^{20}$ 17·11°. Hydrolysis by barium hydroxide and subsequent acidification leads to the formation of *N*-methylmeroquinenine, of which the *picrate*, $C_{16}H_{20}O_9N_4$, decomposes at 218°, and the *picrolonate*, $C_{20}H_{25}O_7N_5$, at 210°; the *ethyl* ester, b. p. 147—148°/22 mm., forms a *hydrochloride*, m. p. 177°; *aurichloride*, m. p. 128—130°; *picrate*, m. p. 102—104°, and *picrolonate*, m. p. 152—154°.

iso*Nitrosoethylcinchotoxine*, $C_{21}H_{25}O_2N_3$, prepared from ethylcinchotoxine, sodium ethoxide, and amyl nitrite, separates from alcohol in slender, white needles, m. p. 136°, and by treatment with phosphorus pentachloride in dry chloroform yields cinchoninic acid and N-*ethylmeroquineninenitrile*, $C_{11}H_{18}N_2$, which is a liquid, b. p. 268°/750 mm., has the odour of piperidine, and is volatile in steam; the *methiodide*, $C_{12}H_{21}N_2I$, decomposes at 230—233°. Hydrolysis of the nitrile yields *N*-ethylmeroquinenine, derivatives of which have been described by Koenigs (*loc. cit.*).

Meroquineninenitrile, $C_9H_{14}N_2$, obtained from *iso*nitrosocinchotoxine in 6—8% yield, b. p. 147—150°/12 mm., is volatile in steam and forms a *picrolonate* decomposing at 215—217°. C. S.

Quinine Formates. Hunkiarbéyendian Lacroix (*J. Pharm. Chim.*, 1906, [vi], **24**, 493—494. See Abstr., 1905, i, 716).—Normal quinine formate loses formic acid towards 50° and yields quinine when heated at 95°; it is dissociated in cold aqueous solution into formic acid and basic quinine formate, m. p. 109° (not 132° as previously stated) $[\alpha]_D^{20}$ −144·2°, which is not affected even by boiling water; it loses, however, the greater part of the acid when heated to just below its melting point. E. F. A.

Alkaloids of Ergot. GEORGE BARGER and HENRY H. DALE (*Arch. Pharm.*, 1906, **244**, 550—555).—Kraft's "hydroergotinine" (Abstr., 1906, i, 979) has already been described as ergotoxine (Barger and Carr, *Chem. News*, 1906, **94**, 89). This alkaloid has the composition $C_{26}H_{30}O_3N_4$ or $C_{27}H_{32}O_3N_4$, and although itself amorphous, forms crystalline salts. Very small doses induced contraction of the pupil, bladder, and uterus in the case of cats, accompanied by abortion if the animal was pregnant; a comparatively large dose induced gangrene in the case of a fowl.

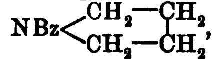
Ergotinine probably has the formula, $C_{28}H_{32}O_4N_4$; it may be the acetyl derivative of ergotoxine. C. F. B.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.*, 1906, **244**, 555—560. Compare Abstr., 1896, i, 710; 1899, i, 92).—Bebeerine has again been isolated from *Radix Pareirae* and also from a commercial specimen of "bebeerinum purum." It had the same melting point and solubility as that obtained previously, but it exhibited dextrorotation, equal in magnitude to the lævorotation of the older specimen, of which it was obviously the optical isomeride. The *benzyl iodide*, $C_{18}H_{21}O_3N,CH_2PhI$, is crystalline and melts at 225°.

When bebeerine, in the process of preparation, is extracted with ether from the crude mass of alkaloid, a resinous mass remains. By extracting this with pyridine and precipitating the solution with methyl alcohol, a small quantity was obtained of an amorphous powder that exactly resembles active bebeerine in composition and reactions, but has m. p. 300° (instead of 214°), and is less soluble in the usual solvents. This substance is precipitated when chloroform solutions of *d*- and *l*-bebeerine are mixed; it is evidently the racemic modification, *r*-bebeerine.

In action on the heart, *d*-bebeerine surpasses *l*-bebeerine greatly. A dose of 0·45 gram of crystalline *d*-bebeerine injected subcutaneously into a rabbit was without effect, whereas the same dose of amorphous *r*-bebeerine killed the animal. C. F. B.

The Phosphorus Haloid Method of Decomposing Pyrrolidine. JULIUS VON BRAUN and ERICH BESCHKE (*Ber.*, 1906, **39**, 4119—4125. Compare Abstr., 1905, i, 596).—This method of decomposing cyclic imines serves as a convenient means of obtaining various dihalogenated paraffins having the substituents attached to the terminal carbon atoms, and the investigation has been extended to pyrrolidine, the simplest five-membered ring compound.

1-*Benzoylpyrrolidine*,  $NBz<\begin{matrix}CH_2—CH_2\\ \quad\;\;|\\ CH_2—CH_2\end{matrix}$, prepared by benzoylating pyrrolidine in cold alkaline solution, is a colourless liquid like glycerol, not miscible with water or dilute acids, b. p. 190—191°/12 mm.

The products of the interaction of phosphorus pentachloride and 1-benzoylpyrrolidine depend on the conditions of experiment. *Benzo-δ-*

chlorobutylamide, $NHBz\cdot[CH_2]_3\cdot CH_2Cl$, is obtained when the mixture is boiled for one hour, and crystallises from ether in snow-white spears, m. p. 48—49°. If, however, the mixture is distilled, a mixture of benzonitrile and *αδ-dichlorobutane* is formed. The latter is a colourless liquid of agreeable aromatic odour, b. p. 53—54°/12 mm., 161—163°/760 mm.

Benzo-δ-iodobutylamide, $NHBz\cdot[CH_2]_3\cdot CH_2I$, is obtained from the corresponding chloro-derivative by digestion with sodium iodide in alcoholic solution. It crystallises from a mixture of ether and light petroleum in slender, colourless needles, m. p. 58°.

The interaction of phosphorus pentabromide and 1-benzoylpyrrolidine gives benzonitrile and αδ-dibromobutane, b. p. 82°/12 mm. (compare Hamonet, Abstr., 1901, i, 247).

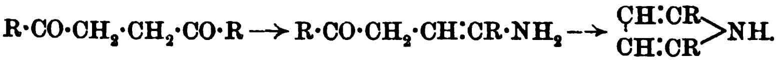
An improved method of preparing pyrrolidine in large quantities is described (compare Gabriel, Abstr., 1892, i, 131); in the course of this preparation a by-product, *λ-phenoxybutyramide*, $OPh\cdot[CH_2]_3\cdot CO\cdot NH_2$, m. p. 80°, crystallising from dilute alcohol in white plates, was isolated.

W. R.

Condensation Products of Pyrroles. GIUSEPPE PLANCHER and ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 447—454. Compare Abstr., 1902, i, 640; 1905, i, 298).—When 2-methylpyrrole is condensed by means of zinc acetate in acetic acid solution, it yields 2 : 4-dimethylindole. The first stage in the change probably consists in the hydrolysis of the 2-methylpyrrole into lævulinaldehyde, which then reacts with a further quantity of 2-methylpyrrole (1 mol.), giving 2 : 4-dimethylindole and 2 mols. of water. 2 : 4-Dimethylindole is also obtained by the condensation of acetone with *m*-tolylhydrazone in presence of zinc chloride and is probably identical with that prepared by Dennstedt (Abstr., 1889, 400).

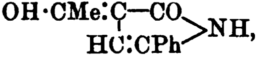
T. H. P.

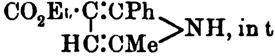
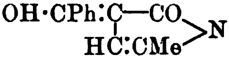
Formation of Pyrrole from 1 : 4-Diketones. Action of Ammonia on Ethyl αβ-Diacylcarboxylic Acids. WALTHER BORSCHE and ALBERT FELS (*Ber.*, 1906, **39**, 3877—3886).—It is probable that in the conversion of 1 : 4-diketones into pyrrole derivatives by means of ammonia, unsaturated 1 : 4-amino-ketones are first formed:



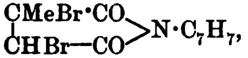
$$R\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot R \longrightarrow R\cdot CO\cdot CH_2\cdot CH{:}CR\cdot NH_2 \longrightarrow \begin{matrix}CH{:}CR\\ CH{:}CR\end{matrix}{>}NH.$$

Knorr and Rabe (Abstr., 1901, i, 163) have isolated ethyl β-amino-Δ^{β}-hexene-3-one-γδ-dicarboxylate from ethyl diacetosuccinate, and the authors have isolated ethyl γ-amino-α-acetyl-γ-phenyl-Δ^{β}-butenoate, $NH_2\cdot CPh{:}CH\cdot CHAc\cdot CO_2Et$, from ammonia and ethyl phenacylacetoacetate in ethereal solution and ethyl γ-amino-α-benzoyl-Δ^{β}-pentenoate, $NH_2\cdot CMe{:}CH\cdot CHBz\cdot CO_2Et$, from ammonia and ethyl acetonylbenzoylacetate.

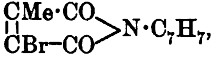
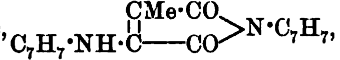
Ethyl γ-amino-α-acetyl-γ-phenyl-Δ^{β}*-butenoate* separates from a mixture of benzene and ether in colourless crystals, m. p. 125—127°. Even when kept in a desiccator water is eliminated and the melting point rapidly falls. When warmed with water or left in contact with dilute alkalis it is partially hydrolysed to ammonia and ethyl phenacylacetoacetate and partially condensed to ethyl 5-phenyl-2-methylpyrrole-3-carboxylate (Paal, Abstr., 1885, 516), which is also formed as a by-product in the preparation of the amino-compound. It is most readily formed by heating the dry amino-compound at 150° or by gently warming with $N/4$ sulphuric acid. When the aminoketone is gently boiled with a $2^{\circ}/_{0}$ solution of sodium hydroxide it yields the *lactam*,  $\begin{array}{l}\mathrm{OH\cdot CMe{:}C{-}CO}\\ \mathrm{HC{:}CPh}\end{array}>\mathrm{NH}$, together with phenyl*cyclo*pentenone (Abstr., 1906, i, 509). The lactam crystallises in greenish-yellow plates, m. p. 158°, decomposing, and is only sparingly soluble in ether. Its *benzoyl* derivative melts and decomposes at 195°.

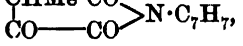
Ethyl γ-amino-α-benzoyl-Δ$^{\beta}$*-pentenoate* forms large colourless, transparent crystals, m. p. 127—128°, and in contact with water is readily hydrolysed. When warmed with dilute sulphuric acid it yields *ethyl 5-phenyl-2-methylpyrrole-4-carboxylate*,  $\begin{array}{l}\mathrm{CO_2Et\cdot C{:}CPh}\\ \mathrm{HC{:}CMe}\end{array}>\mathrm{NH}$, in the form of colourless plates, m. p. 81°. The corresponding acid, m. p. 145°, is extremely unstable and readily loses carbon dioxide yielding 5-phenyl-2-methyl-pyrrole. The *lactam*,  $\begin{array}{l}\mathrm{OH\cdot CPh{:}C{-}CO}\\ \mathrm{HC{:}CMe}\end{array}>\mathrm{NH}$, is obtained together with phenyl*cyclo*pentenone by boiling the amino-ester with $2^{\circ}/_{0}$ sodium hydroxide solution. It crystallises in yellow needles, m. p. 129—130°. J. J. S.

Unsaturated Acids. FRITZ FICHTER (*J. pr. Chem.*, 1906, [ii], **74**, 297—339. Compare Fichter, Enzenauer, and Uellenberg, Abstr., 1900, i, 312; Fichter and Preiswerk, Abstr., 1902, i, 443).—I. *Citraconic acid dibromide and aromatic amines.*—[With ERNST TSCHUDIN.]—*Citracon*-p-*tolylimide dibromide*,



$$\begin{array}{l}\mathrm{CMeBr\cdot CO}\\ \mathrm{CHBr{-}CO}\end{array}>\mathrm{N\cdot C_7H_7},$$

prepared by the action of bromine on citracon-p-tolylimide in glacial acetic solution at 5°, crystallises from alcohol; m. p. 149°. *Bromocitracon*-p-*tolylimide*,  $\begin{array}{l}\mathrm{CMe\cdot CO}\\ \mathrm{CBr{-}CO}\end{array}>\mathrm{N\cdot C_7H_7}$, prepared by heating mesaconic acid dibromide with p-toluidine in aqueous solution on the water-bath, crystallises in small, yellow needles, m. p. 140°. p-*Toluidinocitracon*-p-*tolylimide*,  $\begin{array}{r}\mathrm{CMe\cdot CO}\\ \mathrm{C_7H_7\cdot NH\cdot C{-\!-}CO}\end{array}>\mathrm{N\cdot C_7H_7}$, formed by adding citracon-p-tolylimide to fused p-toluidine at 200°, crystallises in yellow needles, m. p. 177°; when heated with $60^{\circ}/_{0}$ sulphuric acid on the water-bath it yields *methyloxalacetyl*-p-*tolylimide*,



$$\begin{array}{l}\mathrm{CHMe\cdot CO}\\ \mathrm{CO{-\!-}CO}\end{array}>\mathrm{N\cdot C_7H_7},$$

which crystallises from carbon tetrachloride in almost colourless, microscopic needles, m. p. 198—200°, and forms a *silver* salt, $C_{12}H_{10}O_8NAg$, crystallising in yellow needles.

p-*Toluidinosuccin*-p-*tolylimide*, $C_{19}H_{20}O_2N_2$, prepared by reduction of p-toluidinocitracon-p-tolylimide with aluminium amalgam in ethereal solution, crystallises in colourless needles, m. p. 200°. The *stereoisomeride* of this substance which melts at a lower temperature could not be isolated from the mother liquors.

Citracon-o-*tolylimide*, $C_{12}H_{11}O_2N$, crystallises from methyl alcohol in plates, m. p. 64°, and is volatile in a current of steam. *Citracon*-o-*tolylimide dibromide*, $C_{12}H_{11}O_2NBr_2$, forms colourless plates, m. p. 84°. *Bromocitracon*-o-*tolylimide*, $C_{12}H_{10}O_2NBr$, crystallises in slightly yellow needles, m. p. 119°. o-*Toluidinocitracon*-o-*tolylimide*, $C_{19}H_{18}O_2N_2$, separates from alcohol in delicate, yellow, granular crystals, m. p. 138°. o-*Toluidinosuccin*-o-*tolylimide* crystallises from dilute acetic acid in colourless, microscopic needles, m. p. 144°. The *stereoisomeride* of this substance, which melts at a lower temperature, remains in the mother liquors.

Citracon-p-*dimethylaminoanil*, $C_{13}H_{14}O_2N_2$, crystallises in reddish-yellow, glistening needles, m. p. 161·5°. *Bromocitracon*-p-*dimethylaminoanil*, $C_{13}H_{13}O_2N_2Br$, crystallises in slender, yellowish-red needles, m. p. 125°. p-*Dimethylaminoanilinocitracon*-p-*dimethylaminoanil*, $C_{21}H_{24}O_2N_4$, crystallises in brownish-red prisms, m. p. 263—264°.

p-*Dimethylaminoanilinocitraconanil*, $C_{19}H_{19}O_2N_3$, crystallises in red needles, m. p. 163°.

Citracon-a-naphthylimide dibromide, $C_{15}H_{11}O_2NBr_2$, forms a colourless crystalline mass, m. p 161·5—162°. *Bromocitracon-a-naphthylimide*, $C_{15}H_{10}O_2NBr$, crystallises from alcohol in glistening, golden spangles, m. p. 169°.

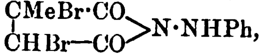
Citracon-β-naphthylimide dibromide forms colourless crystals, m. p. 169·5—170°. *Bromocitracon-β-naphthylimide* crystallises from alcohol in light yellow spangles, m. p. 185°. *β-Naphthylaminocitracon-β-naphthylimide*, $C_{25}H_{18}O_2N_2$, forms silky, yellow needles, m. p. 203°.

II. *Citraconic and mesaconic acid dibromides and aromatic hydrazines*.—[With REINHARD VORTISCH.]—The action of aromatic hydrazines on citraconic and mesaconic acid dibromides leads to the formation of 1-aryl-4-methyl-3-pyrazolones (compare Stolz, Abstr., 1905, i, 942). The following pyrazolones together with the corresponding 4-arylazo-1-aryl-3-methyl-5-pyrazolones have been prepared by this reaction. 1-p-*Tolyl-4-methyl-3-pyrazolone*, $C_{11}H_{12}ON_2$, crystallises in stout needles, m. p. 217°. A product, m. p. 242°, was obtained also from citraconic acid dibromide.

1-p-*Bromophenyl-4-methyl-3-pyrazolone*, $C_{10}H_9ON_2Br$, crystallises in white needles, m. p. 245—246°. 4-*p*-Bromophenylazo-1-*p*-bromophenyl-3-methyl-5-pyrazolone, m. p. 229—230°, is identical with Eibner and Lane's azo-compound, m. p. 227° (Abstr., 1906, i, 613).

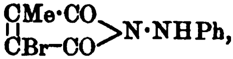
1-p-*Nitrophenyl-4-methyl-3-pyrazolone*, $C_{10}H_9O_3N_3$, crystallises in glistening, slightly brown leaflets, m. p. 266°, and dissolves in dilute sodium hydroxide, forming an intensely red solution.

III. *Action of phenylhydrazine on citraconic acid*.—[With GUSTAV FÜEG.]—*Citraconphenylhydrazone dibromide*,

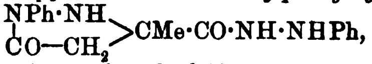


$$\begin{array}{l}\mathrm{CMeBr\cdot CO} \\ \mathrm{CHBr—CO}\end{array}\!\!>\mathrm{N\cdot NHPh},$$

prepared by the action of bromine on citraconphenylhydrazone, crystallises from carbon tetrachloride in yellow aggregates of small needles, m. p. 144°. It readily loses hydrogen bromide, forming *bromocitracon-*

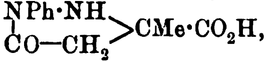
phenylhydrazone,  $\begin{array}{l}\mathrm{CMe\cdot CO}\\ \|\\ \mathrm{CBr{-}CO}\end{array}\!\!>\mathrm{N\cdot NHPh}$, which separates from carbon tetrachloride in yellow crystals, m. p. 136°.

1-*Phenyl*-3-*methyl*-5-*pyrazolidone*-3-*carboxylphenylhydrazide*,



$$\begin{array}{l}\mathrm{NPh\cdot NH}\\ |\\ \mathrm{CO{-}CH_2}\end{array}\!\!>\mathrm{CMe\cdot CO\cdot NH\cdot NHPh},$$

prepared by boiling citraconic anhydride with 2 mols. of phenylhydrazine in aqueous solution, crystallises in glistening, white leaflets, m. p. 144°. It is hydrolysed by much boiling hydrochloric acid, forming 1-*phenyl*-3-*methyl*-5-*pyrazolidone*-3-*carboxylic acid*,



$$\begin{array}{l}\mathrm{NPh\cdot NH}\\ |\\ \mathrm{CO{-}CH_2}\end{array}\!\!>\mathrm{CMe\cdot CO_2H},$$

which crystallises from benzene in broad, colourless needles, m. p. 139°, and is oxidised by ferric chloride to pyrazole blue. The *silver* salt, $C_{11}H_{11}O_3N_2Ag$, is crystalline and forms a silver mirror when heated with a solvent. The action of an excess of nitrous acid on the carboxylic acid leads to the formation of 4-*iso*nitroso-1-phenyl-3-methyl-5-pyrazolone.

Duden's phenylhydrazinesuccinyldihydrazide (Abstr., 1893, i, 231) is considered to be the phenylhydrazide of 1-phenyl-5-pyrazolidone-3-carboxylic acid.

Citracon-p-*tolylhydrazone*, $C_{12}H_{12}O_2N_2$, separates from alcohol in yellow crystals, m. p. 169. 1-p-*Tolyl*-3-*methyl*-5-*pyrazolidone*-3-*carboxyl*-p-*tolylhydrazide*, $C_{19}H_{22}O_2N_4$, crystallises from alcohol in glistening, white leaflets, m. p. 204—206° with slight decomposition. 1-p-*Tolyl*-3-*methyl*-5-*pyrazolidone*-3-*carboxylic acid*, $C_{12}H_{14}O_3N_2$, forms colourless needles, m. p. 148°, and when treated with nitrous acid yields 4-*iso*-nitroso-1-p-tolyl-3-methyl-5-pyrazolone.

Citracon-2 : 4-*xylylhydrazone*, $C_{13}H_{14}O_2N_2$, separates from alcohol in orange-red crystals, m. p. 129°.

Citracon-p-*nitrophenylhydrazone*, $C_{11}H_9O_4N_3$, crystallises in brownish-red needles, m. p. 205°.

IV. *Iodophenylhydrazines*.—[With KARL PHILIPP.]—5-*Iodo*-2-*acetylaminotoluene*, $C_9H_{10}ONI$, prepared by the action of iodine chloride on *o*-acetotoluidide, crystallises in long, glistening, silky needles, m. p. 168°. 5-*Iodo*-2-*aminotoluene*, C_7H_8NI, forms stout, colourless crystals, m. p. 88°. 5-*Iodotolyl*-2-*hydrazine*, $C_7H_9N_2I$, prepared from diazotised 5-iodo-2-aminotoluene by conversion into potassium 5-iodo-toluene-2-diazosulphonate and reduction of this with stannous chloride and hydrochloric acid, crystallises in colourless plates, m. p. 98°.

4-*Iodophenylbenzylidenehydrazine*, $C_{13}H_{11}N_2I$, formed from benzaldehyde and 4-iodophenylhydrazine (Neufeld, Abstr., 1889, 251), crystallises in almost colourless leaflets, m. p. 121°.

Phenyl-4-*iodobenzylidenehydrazine* crystallises in silvery leaflets, m. p. 90°.

2 : 4-*Di-iodophenylbenzylidenehydrazine*, $C_{13}H_{10}N_2I_2$, forms colourless plates, m. p. 104°.

5-*Iodo*-o-*tolylbenzylidenehydrazine*, $C_{14}H_{13}N_2I$, crystallises in silvery plates, m. p. 102—103°.

4′-*Iodoformazylbenzene*, $C_{19}H_{15}N_4I$, formed by the action of diazobenzene on 4-iodophenylbenzylidenehydrazine, crystallises from alcohol or light petroleum, m. p. 185—186°.

Sodium 4′-*iodoformazylbenzenesulphonate*,

$$C_6H_4I\cdot N_2H\text{:}C(N_2Ph)\cdot C_6H_4\cdot SO_3Na,$$

forms a red, crystalline powder and dyes silk a bluish-red.

2′ : 4′-*Di-iodoformazylbenzene*, $C_{19}H_{14}N_4I_2$, crystallises in dark red needles, m. p. 186°.

5′-*Iodo-o-tolylformazylbenzene*, $C_{20}H_{17}N_4I$, forms glistening, black needles, m. p. 167°.

1-p-*Iodophenyl*-3-*methyl*-5-*pyrazolone*, $C_{10}H_9ON_2I$, formed from 4-iodophenylhydrazine and ethyl acetoacetate, crystallises from alcohol in colourless needles, m. p. 196°. The 4-iso*nitroso*-derivative, $C_{10}H_8O_2N_3I$, forms yellow needles, m. p. 189°.

1-*Iodophenyl*-2 : 3-*dimethyl*-5-*pyrazolone* (p-*iodoantipyrine*),

$$C_{11}H_{11}ON_2I,$$

crystallises in colourless needles, m. p. 126°.

1-op-*Di-iodophenyl*-3-*methyl*-5-*pyrazolone*, $C_{10}H_8ON_2I_2$, separates from toluene in a slightly yellow, crystalline crust, m. p. 153°.

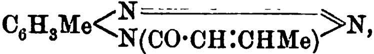
1-*Iodo-o-tolyl*-3-*methyl*-5-*pyrazolone*, $C_{11}H_{11}ON_2I$, m. p. 194°, forms a golden-yellow iso*nitroso*-derivative, $C_{11}H_{10}O_2N_3I$, crystallising in leaflets, m. p. 181°.

1-p-*Iodophenyl*-4-*methyl*-3-*pyrazolone* or 5-*pyrazolone*, $C_{10}H_9ON_2I$, formed from 4-iodophenylhydrazine and mesaconic acid dibromide, crystallises in glistening, silvery leaflets, m. p. 126—127°.

V. *Crotonyltolylenediamine* (compare Autenrieth and Pretzell, Abstr., 1903, i, 474).—[With Ernst Preiswerk.]—*Crotonyl*-p-*toluidide*, $C_{11}H_{13}ON$, formed by heating crotonic acid with *p*-toluidine in a reflux apparatus and distilling the product in a vacuum, crystallises from benzene; m. p. 132°; an excess of *p*-toluidine leads to the formation of *β*-p-*toluidinobutyryl*-p-*toluidide*, $C_{18}H_{22}ON_2$, which crystallises from a mixture of benzene and light petroleum; m. p. 101°. *Dibromobutyryl* p-*toluidide*, $C_{11}H_{13}ONBr_2$, forms slender, white needles, m. p. 171°.

Crotonyl-3-*nitro*-p-*toluidide*, $C_{11}H_{12}O_3N_2$, formed by the action of nitric acid, D 1·45, on crotonyl-*p*-toluidide, crystallises in yellowish-red needles, m. p. 111°. When reduced with tin and hydrochloric acid under cooling, it yields 3-*amino*-4-*crotonylaminotoluene*, $C_{11}H_{14}ON_2$, which forms white needles, m. p. 148°. Energetic reduction of the nitro-compound or boiling of the preceding compound with hydrochloric acid leads to a partial intramolecular change, resulting in the formation of 4-*amino*-3-*crotonylaminotoluene*; this separates from benzene in stout crystals, m. p. 182°.

1-*Crotonyl*-5-*methyl*-1 : 2 : 3-*benzotriazole*,



$$C_6H_3Me{<}\begin{matrix}N\text{=}\text{=}\text{=}\text{=}\text{=}\text{=}\text{=}\text{=}\\ N(CO\cdot CH\text{:}CHMe)\end{matrix}{\gg}N,$$

prepared by the action of nitrous acid on 3-amino-4-crotonylaminotoluene, crystallises in white needles, m. p. 148°.

1-*Crotonyl*-6-*methyl*-1 : 2 : 3-*benzotriazole*, $C_{11}H_{11}ON_3$, prepared from 4-amino-3-crotonylaminotoluidine, crystallises in broad, flat needles, m. p. 186°.

2-Cinnamenyl-5-methylbenziminazole (Bamberger and Berlé, Abstr., 1893, i, 435) is formed by heating cinnamic acid with tolylene-3 : 4-diamine and distilling the product in a vacuum; it crystallises with $\frac{1}{2}H_2O$, m. p. 108—110°, loses $\frac{1}{2}H_2O$ at 130°; the anhydrous base crystallises from dry toluene; m. p. 164—165°. When treated with bromine in chloroform solution, the base forms an orange-yellow *perbromide* which is converted by boiling alcohol into *bromocinnamenylmethylbenziminazole hydrobromide*, $C_{16}H_{13}N_2Br,HBr$, crystallising in colourless needles. The free *bromo*-base, $C_{16}H_{13}N_2Br$, forms colourless crystals, m. p. 195°.

VI. *Methylbenziminazoles from fatty acids.*—[With GEORGE ROSENBERGER.]—Whilst methylbenziminazoles are formed by distillation of acyltolylene-3 : 4-diamines or of tolylene-3 : 4-diamine with α-methyl-Δ^{β}-pentoic acid or cinnamic acid (compare preceding section), only resinous substances are obtained on heating crotonyl- or dimethylacryltolylene-3 : 4-diamines.

Butyryl-p-*toluidide*, $C_{11}H_{15}ON$, forms white, glistening needles, m. p. 73—74°. 3-*Nitrobutyryl*-p-*toluidide*, $C_{11}H_{14}O_3N_2$, crystallises in yellow needles, m. p. 62°. 3-*Amino*-4-*butyrylaminotoluene*, $C_{11}H_{16}ON_2$, forms white leaflets, m. p. 140°. 1-*Butyryl*-5-*methyl*-1 : 2 : 3-*benzotriazole*, $C_{11}H_{13}ON_3$, m. p. 40°. 5-*Methyl*-2-*propylbenziminazole*, $C_{11}H_{14}N_2$, crystallises from water in flat, white needles, m. p. 156—157°.

iso*Valeryl*-p-*toluidide*, $C_{12}H_{17}ON$, forms flat, white needles, m. p. 110°, and on nitration yields 3-nitro-*iso*valeryl-p-toluidide (Friederici, Abstr., 1879, 311). 3-*Amino*-4-iso*valerylaminotoluene*, $C_{12}H_{18}ON_2$, forms white leaflets, m. p. 154°. 1-iso*Valeryl*-5-*methyl*-1 : 2 : 3-*benzotriazole*, $C_{12}H_{15}ON_3$, forms white, nacreous leaflets, m. p. 54°. 5-Methyl-2-*iso*butylbenziminazole crystallises in white needles, m. p. 160° (145—146°, Hübner, Abstr., 1882, 180).

iso*Heptoyl*-p-*toluidide*, $C_{14}H_{21}ON$, crystallises from alcohol in white needles, m. p. 75°. 3-*Nitro*iso*heptoyl*-p-*toluidide*, $C_{14}H_{20}O_3N_2$, forms yellow or colourless needles, m. p. 62°. 3-*Amino*-4-iso*heptoylaminotoluene*, $C_{14}H_{22}ON_2$, crystallises in white leaflets, m. p. 130°. 5-*Methyl*-1-iso*heptoyl*-1 : 2 : 3-*benzotriazole*, $C_{14}H_{19}ON_3$, forms white needles, m. p. 52°. 5-*Methyl*-2-iso*hexylbenziminazole*, $C_{14}H_{20}N_2$, crystallises from alcohol in white needles, m. p. 119°.

Dimethylacryl-p-*toluidide*, $C_{12}H_{15}ON$, crystallises in flat, white needles, m. p. 102°. The 3-*nitro*-derivative, $C_{12}H_{14}O_3N_2$, forms yellowish-red needles, m. p. 131°. 3-*Amino*-4-*dimethylacrylaminotoluene*, $C_{12}H_{16}ON_2$, crystallises in white leaflets, m. p. 133°. 1-*Dimethylacryl*-5-*methyl*-1 : 2 : 3-*benzotriazole*, $C_{12}H_{13}ON_3$, separates from alcohol in long needles, m. p. 129°.

Cinnamoyl-3-*nitrotoluidide*, $C_{16}H_{14}O_3N_2$, forms yellow leaflets, m. p. 147°. 3-*Amino*-4-*cinnamoylaminotoluene*, crystallises in light yellow needles, m. p. 201°. 1-*Cinnamoyl*-5-*methyl*-1 : 2 : 3-*benzotriazole*, $C_{16}H_{13}ON_3$, m. p. 156°.

α-*Methyl*-Δ^{β}-*pentenoyl*-p-*toluidide*, $C_{13}H_{17}ON$, crystallises in white leaflets or scales, m. p. 73°, and on nitration yields a mixture of products (compare Fichter and Pfister, Abstr., 1904, i, 547). 5-*Methyl*-2-α-*methyl*-Δ^{β}-*butenylbenziminazole*, $C_{13}H_{16}N_2$, m. p. 145°, crystallises from water and forms a deep yellow *picrate*.

VII. *Diphenylvinylacetic acid.*—[With WILHELM LATZKO.]—Whilst the relative stabilities of γ-phenylcrotonic and γ-phenylvinylacetic acids towards sodium hydroxide are the converse of those of the Δ^{α}- and Δ^{β}- unsaturated fatty acids in general (Fittig and Luib, Abstr., 1895, i, 223), βγ-diphenyl-crotonic and -vinylacetic acids behave in the normal manner (compare Thiele, Abstr., 1899, i, 217, 612).

βγ-Diphenylvinylacetic acid, $CHPh{:}CPh{\cdot}CH_2{\cdot}CO_2H$, is prepared by heating a mixture of sodium phenylsuccinate, benzaldehyde, and acetic anhydride in a reflux apparatus at 125—130°; it crystallises from a mixture of benzene and light petroleum in slender needles, m. p. 172—173°, and decolorises alkaline potassium permanganate instantaneously. The *calcium* ($4H_2O$) and *barium* ($\frac{1}{2}H_2O$) salts are described.

γ-Bromo-βγ-diphenylbutyric acid, $C_{16}H_{15}O_2Br$, formed by the action of hydrogen bromide on the preceding acid in glacial acetic acid solution, crystallises from a mixture of ether and light petroleum in needles, m. p. 139°, and when boiled with water yields βγ-diphenylvinylacetic acid together with traces of a neutral substance.

βγ-Diphenylcrotonic acid (*β-benzylcinnamic acid*), $C_{16}H_{14}O_2,H_2O$, formed by boiling βγ-diphenyl*iso*crotonic acid with 40 mols. of sodium hydroxide in 20% solution, crystallises from water in glistening leaflets, and loses H_2O at 125°; the anhydrous acid crystallises from a mixture of ether and light petroleum in needles, m. p. 130—131°, and decolorises alkaline potassium permanganate instantaneously.

allo-*βγ-Diphenylvinylacetic acid*, $C_{16}H_{14}O_2$, formed together with βγ-diphenylvinylacetic acid by condensation of ethyl phenylsuccinate and benzaldehyde in presence of sodium ethoxide in absolute ethereal solution, crystallises from a mixture of ether and light petroleum, m. p. 142°, is an extremely weak acid which cannot be titrated sharply (compare Sudborough and Lloyd, Trans., 1898, **73**, 81), decolorises alkaline potassium permanganate instantaneously, and yields β-benzylcinnamic acid when boiled with aqueous sodium hydroxide; the *calcium* salt, $(C_{16}H_{13}O_2)_2Ca,C_{16}H_{14}O_2,7H_2O$, crystallises in needles.

VIII. *Benzylcrotonic acid*.—[With EUGEN ALBER.]—When carefully distilled, β-hydroxy-α-benzylbutyric acid yields α-benzylcrotonic acid and α-phenyl-Δ_{β}-butylene.

α-Benzylcrotonic acid, $CH_2Ph{\cdot}C(CO_2H){:}CHMe$, crystallises from hot water in long, silky, white needles, m. p. 99°, and is slightly volatile in a current of steam. The *magnesium*, *calcium*, and *barium* salts are amorphous and readily soluble. *α-Benzylcrotonyl chloride*, b. p. 139°/12 mm. *α-Benzylcrotonamide*, $C_{11}H_{13}ON$, crystallises from alcohol in slender needles, m. p. 117—118°. The *anilide*, $C_{17}H_{17}ON$, forms white needles, m. p. 90—91°. The p-*toluidide*, $C_{18}H_{19}ON$, crystallises in slender, white needles, m. p. 107°. *β-Bromo-α-benzylbutyric acid*, $C_{11}H_{13}O_2Br$, m. p. 52—55°, formed by the action of hydrogen bromide on α-benzylcrotonic acid in glacial acetic acid solution, could not be purified and yields α-phenyl-Δ^{β}-butylene and α-benzylcrotonic acid when boiled with sodium carbonate solution.

When fused with hydrated potassium hydroxide at 230°, α-benzylcrotonic acid undergoes isomeric changes, forming α-benzylidenebutyric (phenylangelic) acid, m. p. 104—105°, together with traces of hydrocinnamic acid. *α-Benzylidenebutyryl chloride* forms a yellow oil, b. p.

142°/14 mm; the *anilide*, $C_{17}H_{17}ON$, crystallises in white needles, m. p. 128—129°; the p-*toluidide*, $C_{18}H_{19}ON$, forms slender, white needles, m. p. 111°. *β-Bromo-β-phenyl-α-ethylpropionic acid*, $C_{11}H_{13}O_2Br$, formed by the action of hydrogen bromide on α-benzylidenebutyric acid, crystallises in glistening, fatty leaflets, m. p. 135—137°, and yields chiefly α-phenyl-Δ^{β}-butylene and α-benzylidenebutyric acid when boiled with aqueous sodium carbonate. The *magnesium* ($3H_2O$), *calcium* ($4H_2O$), and *barium* ($3H_2O$) salts of α-benzylidenebutyric acid are described.

When boiled with 10 vols. of 20% alcoholic potassium hydroxide, α-phenyl-Δ^{β}-butylene is converted almost quantitatively into α-phenyl-Δ^{α}-butylene.

γ-Phenylvinylacetic acid is formed in a 50—55% yield by boiling phenylacetaldehyde with malonic acid and pyridine in a reflux apparatus, or by heating phenylacetaldehyde with ethyl malonate and glacial acetic acid on the water-bath; in both methods a small amount of phenylcrotonic acid is formed. G. Y.

Palladium Halides. ALEXANDER GUTBIER and M. WOERNLE (*Ber.*, 1906, **39**, 4134—4139. Compare Abstr., 1905, i, 584, 876; ii, 534; 1906, i, 12, 244, 402, 805).—The authors have prepared pyridinium, α-picolinium, and quinolinium tetrahalogen palladium salts and examined their behaviour towards water.

The salts in question are sparingly soluble in alcohol, and may be crystallised from the corresponding halogen acids without undergoing decomposition. Their aqueous solutions undergo slow decomposition at the ordinary temperature and rapid decomposition when warmed with the formation of palladosammines.

The Anderson reaction is always observed when palladous halides unite with halogen hydrates of aromatic bases or of aliphatic diamines to form more complex compounds; the reaction is not, however, noted when the halogen hydrates of aliphatic amines are used.

Pyridiniumpalladochloride, $(C_5H_5N)_2,H_2PdCl_4$, separates from dilute hydrochloric acid in brownish-yellow needles. By the action of water, it is converted into *palladous pyridine chloride*, $Pd(C_5H_5N)_2Cl_2$, which is a yellow, microcrystalline powder. *Pyridiniumpalladichloride*, $(C_5H_5N)_2,H_2PdCl_6$, forms red prisms.

Pyridiniumpalladobromide, $(C_5H_5N)_2,H_2PdBr_4$, crystallises from dilute hydrobromic acid in reddish-brown leaflets and by the action of water is converted into *palladous pyridine bromide*, $Pd(C_5H_5N)_2Br_2$, which is a yellow, microcrystalline powder. *Pyridiniumpalladibromide*, $C_5H_5N)_2,H_2PdBr_6$, forms bluish-black prisms.

α-Picoliniumpalladochloride, $(C_5H_4NMe)_2,H_2PdCl_4$, separates from dilute hydrochloric acid in brown needles and forms with water *palladous α-picoline chloride*, $Pd(C_5H_4NMe)_2Cl_2$, which separates from alcohol in yellow leaflets. The *palladichloride*, $(C_5H_4NMe)_2,H_2PdCl_6$, forms red prismatic needles. The *palladobromide*, $(C_5H_4NMe)_2,H_2PdBr_4$, separates from dilute hydrobromic acid in brown needles. It is converted by water into *palladous α-picoline bromide*, $Pd(C_5H_4NMe)_2Br_2$, which crystallises in yellowish-red leaflets.

Quinoliniumpalladochloride, $(C_9H_7N)_2,H_2PdCl_4$, separates from dilute hydrochloric acid in yellowish-brown needles, and is converted by water into *palladous quinoline chlorine*, $Pd(C_9H_7N)_2Cl_2$, which is a yellow solid.

Quinoliniumpalladichloride, $(C_9H_7N)_2,H_2PdCl_6$, forms red prisms.

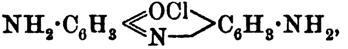
Quinoliniumpalladobromide, $(C_9H_7N)_2,H_2PdBr_4$, crystallises from dilute hydrobromic acid in reddish-brown needles, and with water forms *palladous quinoline bromide*, $Pd(C_9H_7N)_2Br$, which forms reddish-brown leaflets.

Methylammoniumpalladichloride, $(NH_2Me)_2,H_2PdCl_6$, forms brick-red leaflets and needles; the *palladibromide* forms green needles.

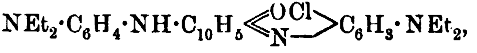
Ethylammoniumpalladichloride, $(NH_2Et)_2,H_2PdCl_6$, crystallises in scarlet needles.

Ethylammoniumpalladibromide, $(NH_2Et)_2,H_2PdBr_6$, forms green needles. *Propylammoniumpalladibromide*, $(NH_2Pr)_2,H_2PdCl_6$, forms brick-red leaflets; the *palladibromide* forms dark bluish-green leaflets and needles.

iso*Butylammoniumpalladichloride*, $(C_4H_9\cdot NH_2)_2,H_2PdCl_6$, forms leaflets with a bronze lustre; the *palladibromide* separates in bluish-black needles. A. McK.

Oxazine Dyes. JULIUS FORMÁNEK (*Zeit. Farb. Ind.*, 1906, **5**, 433—434).—A preliminary notice. *Diaminophenazoxonium chloride*,  $NH_2\cdot C_6H_3<\overset{OCl}{\underset{N}{—}}>C_6H_3\cdot NH_2$, is prepared by adding *m*-aminophenol to *p*-benzoquinonedichlorodi-imine in glacial acetic acid solution. The analogous methyl, ethyl, dimethyl, and diethylaminophenazoxonium compounds were prepared similarly, using the corresponding alkylaminophenols. *Trimethyldiaminophenazoxonium chloride* when prepared from nitrosomethylaniline and *m*-dimethylaminophenol is always mixed with the tetramethyl compound; it is obtained pure only by the interaction of methylaniline and nitroso-*m*-dimethylaminophenol in acetic acid solution. Similar remarks apply to the analogous triethyldiaminophenazoxonium chloride.

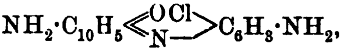
Diethylaminophenazoxonium chloride is prepared by gently warming a 1 : 20 solution of nitrosoethylaniline hydrochloride and β-naphthol; if more concentrated solutions are used at a higher temperature the initial product condenses with *p*-phenylenediethyldiamine, formed from the nitrosodiethylaniline, and a greater or less proportion of *diethylamino diethylanilinoaminophenonaphthazoxonium chloride*,



$$NEt_2\cdot C_6H_4\cdot NH\cdot C_{10}H_5<\overset{OCl}{\underset{N}{—}}>C_6H_3\cdot NEt_2,$$

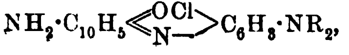
is produced according to the conditions. Similar results are obtained with nitrosodimethylaniline and β-naphthol.

Diaminophenonaphthazoxonium chloride,



$$NH_2\cdot C_{10}H_5<\overset{OCl}{\underset{N}{—}}>C_6H_3\cdot NH_2,$$

prepared by warming a concentrated aqueous solution of aminophenonaphthazoxonium chloride with hydroxylamine hydrochloride, forms brown crystals with a bronze reflex and gives fluorescent solutions. Methyl-Nile-blue and ethyl-Nile-blue,



$$NH_2\cdot C_{10}H_5<\overset{OCl}{\underset{N}{—}}>C_6H_3\cdot NR_2,$$

can be readily prepared in a similar way from Meldola's Blue or diethylaminophenonaphthazoxonium chloride respectively by using hydroxylamine.

The spectroscopic relations of the foregoing substances will be dealt with subsequently. W. A. D.

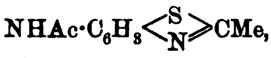
Sulphineazo-dyes. HERMANN A. MÜLLER (*Zeit. Farb. Ind.*, 1906, **5**, 357—361).—On reduction with ammonium sulphide, 2 : 4-dinitro-1-thiocyanobenzene (Austen and Smith, Abstr., 1886, 693) is converted into 2 : 2'-*dinitro*-4 : 4'-*diaminodiphenyl disulphide*,

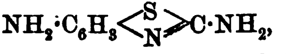
$$S_2[C_6H_3(NO_2)\cdot NH_2]_2,$$

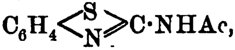
which crystallises from alcohol in lustrous red leaflets, m. p. 222°; the nitro-group in the para-position to the thiocyano-radicle is therefore reduced, not that in the ortho-position. It is probable that a mercaptan is the primary product of the reduction, but it undergoes oxidation during the treatment employed. The structure of the product follows from its giving 2 : 2'-dinitrodiphenyl disulphide (Cleve, Abstr., 1887, 834) on eliminating the amino-groups by the diazo-reaction; the 2 : 2'-dinitrodiphenyl sulphide was characterised by its giving, on reduction, 2 : 2'-diaminodiphenyl disulphide and by its conversion into 1-methylbenzothiazole.

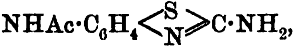
2 : 2'-Dinitro-4 : 4'-diaminodiphenyl disulphide is used for preparing dyes by diazotising and coupling with bases (French Patent, 337329, 1903). 2 : 2'-*Dinitrodiphenyl disulphide*-4 : 4'-*disazo-di-β-naphthylamine*, $[NH_2\cdot C_{10}H_6\cdot N_2\cdot C_6H_3(NO_2)]_2S_2$, prepared in this way from β-naphthylamine, separates from acetic acid as a dark red crystalline powder.

p-*Nitrothiocyanobenzene*, $NO_2\cdot C_6H_4\cdot CNS$, prepared from *p*-nitroaniline by the diazo-reaction, crystallises from carbon tetrachloride in lustrous leaflets, from glacial acetic acid in long, white needles, m. p. 133°. On reduction with ammonium sulphide it gives 4 : 4'-dinitrodiphenyl sulphide, which is reduced by stannous chloride to the corresponding 4 : 4'-diamino-compound; this serves to prepare *diphenyldisulphide*-4 : 4'-*disazo-di-β-naphthylamine*, $[NH_2\cdot C_{10}H_6\cdot N_2\cdot C_6H_3]_2S_2$, as above; the dye crystallises from toluene in dark red crystals.

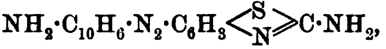
On reduction with stannous chloride and hydrochloric acid, 2 : 2'-dinitro-4 : 4'-diaminodiphenyl disulphide gives 2 : 4-*diaminothiophenol hydrochloride*; on decomposing this with ammonia, 2 : 4 : 2' : 4'-*tetra-aminodiphenyl disulphide*, $S_2[C_6H_3(NH_2)_2]_2$, is obtained, which crystallises from benzene or toluene, m. p. 148°. When the reduction of 2 : 2'-dinitro-4 : 4'-diaminodiphenyl disulphide is effected by zinc dust in presence of acetic acid and acetic anhydride, 4-*acetylamino*-1-*methylbenzothiazole*,  $NHAc\cdot C_6H_3{<}\substack{S\\N}{>}CMe$, is obtained; it crystallises from water in nearly colourless needles, m. p. 159°.

On reduction with stannous chloride and hydrochloric acid, 2 : 4-dinitro-1-thiocyanobenzene gives, not the corresponding diamino-derivative (compare Austen, Abstr., 1889, 700), but the isomeric 1 : 4-*diaminobenzothiazole*,  $NH_2\cdot C_6H_3{<}\substack{S\\N}{>}C\cdot NH_2$, which crystallises from toluene or benzene in silvery leaflets, m. p. 175°. The reduction of *o*-nitrothiocyanobenzene takes place similarly. o-*Nitrothiocyano*-

benzene, $NO_2\cdot C_6H_4\cdot CNS$, prepared from diazotised *o*-nitroaniline and potassium thiocyanate, crystallises from carbon tetrachloride in colourless needles, m. p. 132·5°; on reduction with stannous chloride and hydrochloric acid it gives 1-aminobenzothiazole, the *acetyl* derivative,  $C_6H_4<\substack{S\\N}>C\cdot NHAc$, of which forms white crystals, m. p. 185—186°.

1 : 4-*Diacetyldiaminobenzothiazole*, prepared by boiling the corresponding diamino-compound with acetic anhydride and acetic acid, separates from the latter in white crystals containing $1\frac{1}{2}$ mol. of acetic acid, m. p. 271°. When the acetylation is carried out in alcoholic solution at the ordinary temperature, 1-*amino*-4-*acetylaminobenzothiazole*,  $NHAc\cdot C_6H_4<\substack{S\\N}>C\cdot NH_2$, m. p. 259—261°, is formed; it crystallises from acetic acid on adding light petroleum.

1-*Aminobenzothiazole*-4-*azo*-β-*naphthylamine*,

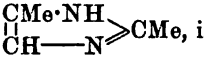


$$NH_2\cdot C_{10}H_6\cdot N_2\cdot C_6H_3<\substack{S\\N}>C\cdot NH_2,$$

prepared by diazotising 1-4-diaminobenzothiazole and coupling with β-naphthylamine, crystallises from alcohol in dark violet needles with a metallic reflex, from toluene in reddish-yellow leaflets; m. p. 223°.

W. A. D.

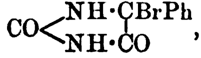
Decomposition of Dextrose by Ammoniacal Zinc Hydroxide in the Presence of Acetaldehyde.

ADOLF WINDAUS (*Ber.*, 1906, **39**, 3886—3891. Compare Abstr., 1905, i, 381).—2 : 4-*Dimethylglyoxaline*,  $\begin{matrix}CMe\cdot NH\\ \| \\ CH\text{——}N\end{matrix}\!>CMe$, is formed together with the 4-methyl compound when dextrose is left for some time in contact with an ammoniacal solution of zinc hydroxide and concentrated acetaldehyde solution. The 4-methylglyoxaline only is formed in the absence of acetaldehyde. The two bases are separated by means of their oxalates, as the dimethylglyoxaline oxalate dissolves readily in methyl alcohol. The *picrate*, $C_{11}H_{11}O_7N_5$, crystallises from hot water in deep yellow prisms, m. p. 142—143°, and is less soluble in water than the picrate of the monomethylglyoxaline. The base has b. p. 266°/733 mm., m. p. 92°, and dissolves readily in alcohol or water. The *hydrochloride*, $C_5H_9N_2Cl$, m. p. 205°, is hygroscopic. The *platinichloride* melts and decomposes at 204° and the *nitrate* at 133—134°. The constitution of the base follows from the fact that it can be obtained by passing Jowett and Potter's 3 : 4-dimethylglyoxaline (Trans., 1903, **83**, 464) through a strongly heated glass tube (compare Wallach, Abstr., 1883, 910).

J. J. S.

Action of Bromine on α-Lactylcarbamide and Related Compounds. II.

SIEGMUND GABRIEL (*Annalen*, 1906, **350**, 118—134. Compare Abstr., 1906, i, 634).—The action of bromine on α-phenylhydantoin does not lead to the formation of products analogous to those obtained from 4-methylhydantoin (α-lactylcarbamide).

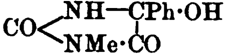
4-*Bromo*-4-*phenylhydantoin*,  $CO<\begin{matrix}NH\cdot CBrPh\\ | \\ NH\cdot CO\end{matrix}$, obtained from 1 mol.

of phenylhydantoin and bromine (> 1 mol.) in glacial acetic acid on the water-bath, forms stout prisms or oblong plates, m. p. >200°, decomposing, loss of hydrogen bromide commencing at 100°. The halogen is very readily displaced. Hot water causes the separation of 4-hydroxy-4-phenylhydantoin, which readily reacts with hydrogen bromide to re-form the bromo-compound. The position of the hydroxyl group or of the halogen atom in these compounds is ascertained by decomposing them with hydrochloric acid at 160°, whereby benzoylformic acid is produced.

4-*Amino*-4-*phenylhydantoin* sinters at 160°, m. p. 285°, decomposing, dissolves in acids or alkalis, yields the hydroxy-compound with boiling water and forms a sparingly soluble *nitrate*, $C_9H_9O_2N_3,HNO_3$, m. p. 199—200°.

4-*Anilino*-4-*phenylhydantoin* forms slender, flattened needles and has m. p. 295—300°, decomposing.

4-Phenyl-1-methylhydantoin by bromination yields the 4-bromo-compound which is converted by hot water into 4-*hydroxy*-4-*phenyl*-1-*methylhydantoin*,

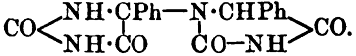


$CO<\begin{array}{l}NH-CPh\cdot OH\\ NMe\cdot CO\end{array}$

, m. p. 128—129°.

The reaction between alcoholic potash, methylamine hydrochloride, and mandelonitrile at 70—80° yields phenylsarcosinamide, the hydrochloride of which and potassium cyanate yield 4-*phenyl*-3-*methylhydantoin*, $C_{10}H_{10}O_2N_2$, which separates from hot water in long needles, m. p. 177°, and dissolves in alkali hydroxides. The 4-*hydroxy*-compound, $C_{10}H_{10}O_3N_2$, has m. p. 167—168°. By methylation, the preceding hydantoin yields 4-*phenyl*-1 : 3-*dimethylhydantoin*, $C_{11}H_{12}O_2N_2$, which separates from water in short, stout, hexagonal prisms, is insoluble in alkalis, and has m. p. 108—109°.

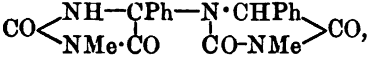
By treating 4-phenylhydantoin with bromine ($\frac{1}{2}$ mol.) in glacial acetic acid at 100°, by heating the same substance with its bromo-derivative, or by heating it with its hydroxy-derivative at 160° or in aqueous or acid solution, a substance, *diphenylhydantil*, is obtained to which is ascribed the constitution



$CO<\begin{array}{l}NH\cdot CPh-N\cdot CHPh\\ NH\cdot CO\quad CO-NH\end{array}>CO.$

It is a microcrystalline powder, m. p. 336—338°, decomposing, sparingly soluble in solvents with high boiling points, but readily in alkalis. Its constitution follows from the decomposition by concentrated hydrochloric acid at 165°, whereby benzoylformic and phenylaminoacetic acids are the characteristic products.

4 : 4′-*Diphenyl*-1 : 1′-*dimethylhydantil*,



$CO<\begin{array}{l}NH-CPh-N\cdot CHPh\\ NMe\cdot CO\quad CO-NMe\end{array}>CO,$

resulting by the methylation of diphenylhydantil or by the bromination of 4-phenyl-1-methylhydantoin in glacial acetic acid, forms long, white needles, m. p. 329—334°, decomposing, does not dissolve in cold alkalis and is decomposed by boiling potash, yielding benzoylformic acid and 4-phenyl-1-methylhydantoin.

When 4-phenyl-3-methylhydantoin, 4-phenyl-1-methylhydantoin, or 4-phenyl-1 : 3-dimethylhydantoin is heated with 4-bromo-4-phenylhydantoin in glacial acetic acid at 100°, diphenylhydantil is obtained contrary to expectation, whilst in the second case diphenyldimethylhydantil is also produced.

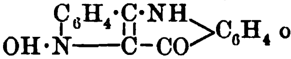
Diphenylhydantil is identical with Pinner's ψ-phenylhydantoin (compare following abstract), which can be obtained also by exposing an alcoholic solution of 4-phenylhydantoin to atmospheric oxygen.

C. S.

ψ-Hydantoins. Adolf Pinner (*Annalen*, 1906, **350**, 135—140. Compare Abstr., 1888, 1102; preceding abstract).—The author has re-examined the decomposition of 4-phenyl-1-ethyl-ψ-hydantoin by barium hydroxide, and has identified ammonia, ethylamine, benzoylformic and 4-phenyl-1-ethylhydantoic acids in the decomposition products. He agrees with Gabriel that phenyl-ψ-hydantoin is diphenylhydantil; similarly, styryl-ψ-hydantoin is dicinnamylhydantil.

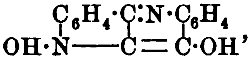
C. S.

Quindoline. Friedrich Fichter and Rudolf Boehringer (*Ber.*, 1906, **39**, 3932—3942).—With the view of obtaining cyclic azoxy-compounds, ethyl *bis-o*-nitrobenzylmalonate was acted on by alcoholic sodium hydroxide. The action was a vigorous one, attended with the separation of sodium carbonate and the formation of a dark red sodium salt, which, when decomposed with acids, formed a compound, $C_{15}H_{10}O_2N_2$. The latter is not, however, an azoxy-compound, but is *dihydroxyquindoline*,



$$\begin{array}{l} C_6H_4\cdot C\cdot NH \\ OH\cdot N\text{——}C-CO \end{array}\!\!>C_6H_4$$

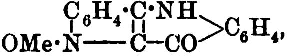
or



$$\begin{array}{l} C_6H_4\cdot C{:}N\cdot C_6H_4 \\ OH\cdot N\text{——}C=C\cdot OH \end{array}$$

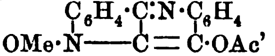
a compound containing both a quinoline and an indene nucleus. Its formation is represented by the equation $C_{21}H_{22}O_8N_2 = C_{15}H_{10}O_2N_2 + 2CO_2 + 2EtOH$; it is assumed that bis-*o*-nitrobenzylmethane is formed as an intermediate product. Dihydroxyquindoline forms a red, crystalline powder which does not melt below 300°; it is a weak acid, dissolving readily in alkali hydroxides, but with difficulty in sodium carbonate or ammonia. It forms dark red salts which are soluble in water.

The acid character of dihydroxyquindoline is ascribed to the hydroxy-group attached to nitrogen, whilst in the other portion of the molecule the grouping is analogous to that in hydroxy-2-methylquinoline. The *methyl ether*,



$$\begin{array}{l} C_6H_4\cdot C\cdot NH \\ OMe\cdot N\text{——}C-CO \end{array}\!\!>C_6H_4$$

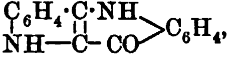
obtained by the action of methyl sulphate on the solution of dihydroxyquindoline in sodium hydroxide, separates in needles, m. p. 184°; it is insoluble in alkali. When acetylated it forms *acetyldihydroxyquindoline methyl ether*,



$$\begin{array}{l} C_6H_4\cdot C{:}N\cdot C_6H_4 \\ OMe\cdot N\text{——}C=C\cdot OAc \end{array}$$

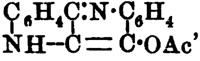
which separates from absolute alcohol in greenish-white needles, m. p. 148°. It is readily saponifiable, and is comparable with esters of hydroxyquinaldine.

When dihydroxyquindoline is warmed with phenylhydrazine it loses one-half of its oxygen and forms *hydroxyquindoline*,



$$\begin{array}{l} C_6H_4\cdot C\cdot NH \\ NH—C-CO \end{array}\!\!>C_6H_4,$$

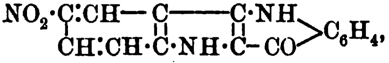
which forms yellow, rhombic crystals and does not melt below 300°; it is a weak base. The *hydrochloride*, $(C_{15}H_{10}ON_2)_2,HCl$, forms yellow, silky needles; the *picrate* is also described. The *acetyl* derivative,



$$\begin{array}{l} C_6H_4C{:}N\cdot C_6H_4 \\ NH—C=C\cdot OAc \end{array},$$

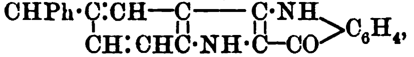
separates from absolute alcohol in yellowish-white needles and is readily saponifiable.

Nitrohydroxyquindoline,



$$\begin{array}{l} NO_2\cdot C{:}CH—C——C\cdot NH \\ CH{:}CH\cdot C\cdot NH\cdot C-CO \end{array}\!\!>C_6H_4,$$

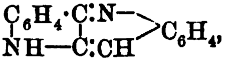
obtained by nitrating hydroxyquindoline in glacial acetic acid solution, separates from nitrobenzene in glistening, red leaflets. Its solution in concentrated sulphuric acid is red, whilst its solution in alcoholic sodium hydroxide is blue. When reduced by sodium sulphide it forms *aminohydroxyquindoline*, $C_{15}H_{11}ON_3$, which separates in yellow needles, forms a *hydrochloride*, and condenses with benzaldehyde to form *benzylideneaminohydroxyquindoline*,



$$\begin{array}{l} CHPh\cdot C{:}CH—C——C\cdot NH \\ CH{:}CHC\cdot NH\cdot C—CO \end{array}\!\!>C_6H_4,$$

which crystallises in needles.

Quindoline,



$$\begin{array}{l} C_6H_4\cdot C{:}N— \\ NH—C{:}CH \end{array}\!\!>C_6H_4,$$

obtained by the vigorous reduction of dihydroxyquindoline by phenylhydrazine, or better by heating dihydroxyquindoline with a mixture of hydriodic acid and phosphorus at 150°, separates from alcohol in colourless needles, m. p. 247—248°; it forms coloured salts. The *hydrochloride*, *hydriodide*, *nitrate*, and *picrate* are described. *Acetylquindoline*, $C_{17}H_{12}ON_2$, separates from alcohol in yellowish-white needles, m. p. 177—178°.

Quindoline methiodide, $C_{16}H_{13}N_2I$, separates from water in yellow needles. It forms a *periodide*, $C_{16}H_{13}N_2I_3$, obtained as a by-product in the preparation of the methiodide, or by heating dihydroxyquindoline with a mixture of methyl iodide and methyl alcohol at 130—140°, and forms glistening leaflets.

Quindoline ethiodide, $C_{17}H_{15}N_2I$, forms yellow needles, m. p. 222—223°; its *periodide*, $C_{17}H_{15}N_2I_3$, separates from alcohol in greenish-black needles.

When a warm aqueous solution of quindoline methiodide is acted on by an excess of a 10°/₀ solution of sodium hydroxide, a product is precipitated which, when crystallised from toluene, is free from iodine. It decomposes at 260°; it is a *pseudo*-base, forming the yellow quaternary salts with acids, even with carbon dioxide. The compound is possibly *methylquindolanol*, $C_{16}H_{14}ON_2$. A. McK.

Basic Triphenylmethane Dyes containing Sulphur. JULIUS SCHMIDLIN (*Ber.*, 1906, **39**, 4204—4216).—When *p*-leucaniline or its homologues (compare D.R.-P. 100556) is treated with fuming sulphuric acid at low temperatures for from eight days to a month and the product is oxidised, best electrolytically, sparingly soluble blue dyes are obtained, which contain two sulphone groups (hence called rosaniline-disulphones), are mono-acid bases, and have two diazotisable amino-groups. p-*Rosanilinedisulphone*, obtained from *p*-leucaniline hydrochloride, forms copper-coloured crystals soluble in acids; the ***sulphate***, $[C_{19}H_{14}N_3(SO_2)_2]_2SO_4,H_2O$, was prepared.

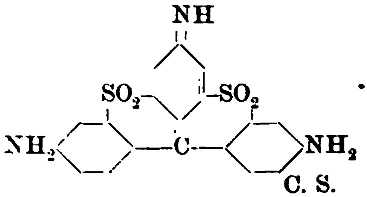
p-*Rosanilinedisulphone trisulphonic acid*, $C_{19}H_{10}N_3(SO_2)_2(SO_3H)_3,4H_2O$, is obtained when *p*-leucaniline hydrochloride and fuming sulphuric acid (60°/₀ of trioxide) are heated to incipient ebullition for two and a half hours. It is a white powder, soluble in warm water to an intensely blue solution, from which concentrated sulphuric acid reprecipitates the hydrated substance in white needles; at 130—140° the water is expelled and the dark brown residue dissolves in water to a blue solution. The alkali salts are colourless. At 170—180° the sulphonic acid absorbs oxygen, changing into a sparingly soluble substance.

Leucaniline hydrochloride yields a similar dye which forms dark blue crystals with red reflex; the *sulphate*, $[C_{20}H_{16}N_3(SO_2)_2]_2SO_4,H_2O$, was prepared.

The leuco-compound of new magenta (triaminotritolylmethane hydrochloride) yields the *sulphate* of *new magenta disulphone*, $[C_{22}H_{20}N_3(SO_2)_2]_2SO_4,H_2O$, which is sparingly soluble in water and separates from 10°/₀ sulphuric acid in dark blue crystals with a red reflex. The *base*, $C_{22}H_{19}N_3(SO_2)_2,H_2O$, is a black, microcrystalline powder, insoluble in water. The *hydrochloride*, $C_{22}H_{19}N_3(SO_2)_2,HCl$, forms brown crystals, is sparingly soluble in water, and does not yield triacid salts.

When new magenta disulphone is boiled with hydrochloric acid for two days the blue colour disappears, and a brown, flocculent *substance*, $C_{22}H_{21}O_8NS_2$, is obtained, which dissolves sparingly in dilute acids, readily in alkalis. New magenta disulphone sulphate is converted by nitrous acid into a *substance* apparently identical with the preceding; the violet-coloured solution of the diazonium salt is extraordinarily sensitive to light, exposure for a few seconds to sunlight causing the evolution of nitrogen and the formation of the substance mentioned above.

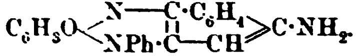
The formula proposed for the rosaniline disulphones is



C. S.

Action of Hydroxylamine on *iso*Rosindone and Thiorosindone, and the Formation of Naphthasafranol from *iso*-Rosindone.

Otto Fischer and K. Arntz (*Ber.*, 1906, **39**, 3807—3812. Compare Fischer and Hepp, Abstr., 1905, i, 948).—The supposed *iso*rosindoneoxime (Fischer and Hepp, Abstr., 1900, i, 461) is now shown to be *s*-amino*iso*rosindone.



$$C_6H_3O\Big\langle\begin{matrix}N\text{——}C\cdot C_6H_4\\ \qquad\;\; \| \\ NPh\cdot C\text{——}CH\end{matrix}\Big\rangle C\cdot NH_2.$$

An improved method for the preparation of the substance is described. *Acetylaminoisorosindone*, $C_{24}H_{17}O_2N_3$, crystallises in steel-blue, glistening needles, dissolves in alcohol, forming a scarlet solution, and gives a bluish-violet coloration with concentrated sulphuric acid. The *benzylidene* derivative, $C_{29}H_{19}ON_2$, formed by heating a molecular mixture of benzaldehyde and amino*iso*rosindone on the water-bath, is obtained in scarlet crystals, gives a violet coloration with concentrated sulphuric acid, and is hydrolysed by boiling dilute acids, forming its generators. The p-*nitrobenzylidene* derivative, $C_{29}H_{18}O_3N_4$, crystallises in red needles. The o-*hydroxybenzylidene* derivative forms scarlet crystals.

When heated with concentrated hydrochloric acid and glacial acetic acid at 180—190° under pressure, amino*iso*rosindone yields the *hydrochloride* of the corresponding hydroxy*iso*rosindone; this forms dark red, metallic needles and remains unchanged when heated with hydrochloric acid at 200—220° under pressure for twenty hours. *Hydroxyisorosindone*, $C_{22}H_{14}O_2N_2$, crystallises from a mixture of benzene and alcohol in glistening, bronze, narrow leaflets, sinters at 230°, and decomposes yielding a red sublimate at 260°. When boiled with alcoholic potassium hydroxide and methyl or ethyl iodide, hydroxy*iso*rosindone yields the corresponding ether of napthasafranol.

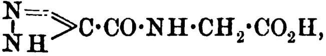
The substance previously described as 7-*o*-tolyl*iso*rosindoneoxime (Abstr., 1900, i, 460) must be amino-*o*-tolyl*iso*rosindone.

The action of hydroxylamine on thiorosindone leads to the formation of Kehrmann and Locher's product, $C_{22}H_{15}ON_3$ (Abstr., 1899, i, 82), which when treated with concentrated hydrochloric acid at 200° under pressure yields rosindone.

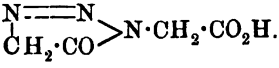
Naphthasafranol is formed when *iso*rosindone is heated with glacial acetic and concentrated hydrochloric acids at 200° under pressure for ten to fifteen hours. G. Y.

Formation of 5-Triazolone and of 5-Triazolone Derivatives from Diazoaliphatic Acids.

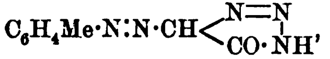
Theodor Curtius and James Thompson (*Ber.*, 1906, **39**, 4140—4144. Compare Abstr., 1906, i, 940, this vol., i, 21).—The authors prove that the compound originally described as *iso*diazoacetylaminoacetic acid,



$$\left.\begin{matrix}N=\\ \mid\\ NH\end{matrix}\right>C\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

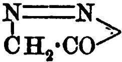
is in reality 5-*triazolone*-1-*acetic acid*,  $\left.\begin{matrix}N{=\!=}N\\ \mid\\ CH_2\cdot CO\end{matrix}\right>N\cdot CH_2\cdot CO_2H$. The isolation of 5-triazolone is described.

When diazoacetamide (1 mol.) is agitated with 2*N*-potassium hydroxide (2 mols.), neither nitrogen nor an appreciable amount of ammonia is evolved. On the addition of a diazotoluene sulphate solution, an orange-coloured solution is obtained, from which, on the addition of acetic acid, 4-*azotoluene*-5-*triazolone*,

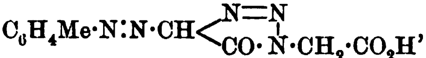


$$C_6H_4Me\cdot N\colon N\cdot CH\left<\begin{matrix}N{=\!=}N\\ \quad\ \mid\\ CO\cdot NH\end{matrix}\right.,$$

is precipitated; it crystallises from alcohol in yellow needles which deflagrate at 163°.

When an aqueous solution of diazoacetamide is warmed with barium hydroxide, the transformation into triazolone also occurs. After removal of the excess of barium hydroxide, the barium salt of triazolone is obtained in needles, from which 5-*triazolone*,  $\begin{array}{l}N{=\!=}N\\ CH_2\cdot CO\end{array}\!\!>NH$, itself may be prepared. The latter separates from dilute alcohol in colourless rosettes and decomposes at about 135°. It gives an acid reaction towards litmus. When boiled with moderately concentrated sulphuric acid, it is decomposed with the gradual evolution of nitrogen, and when alkali is then added, ammonia is evolved. When sodium nitrite and acetic acid are added to its aqueous solution, a dark violet coloration is produced. 5-Triazolone is very stable towards alkali, no ammonia being evolved when it is boiled with concentrated sodium hydroxide.

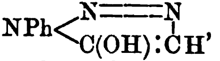
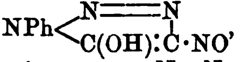
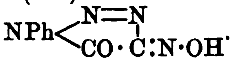
4-*Azotoluene*-5-*triazolone*-1-*acetic acid*,



$$C_6H_4Me\cdot N{:}N\cdot CH<\begin{array}{l}N{=}N\\ CO\cdot N\cdot CH_2\cdot CO_2H\end{array},$$

prepared by coupling 5-triazolone-1-acetic acid, formerly described as *iso*diazoacetylaminoacetic acid (*loc. cit.*), with diazotoluene sulphate, separates from alcohol in orange-red needles, m. p. 156°, decomposing.

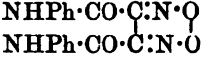
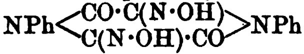
The *amide* separates from alcohol in yellowish-red needles, m. p. 166°, decomposing. Its solution in alkali is yellow. When crystallised from glacial acetic acid, it forms the isomeric *compound*, $C_{11}H_{12}O_2N_6$, which crystallises in colourless needles, m. p. 231°, decomposing, and is insoluble in alkali. A. McK.

Formation of Derivatives of Oxanilhydroxamic Acid from 4-*iso*Nitroso-1-phenyl-5-triazolone. OTTO DIMROTH and LUDWIG TAUB (*Ber.*, 1906, **39**, 3912—3920. Compare Abstr., 1903, i, 127).—By the action of nitrous acid on 5-hydroxy-1-phenyl-1 : 2 : 3-triazole,  $NPh<\begin{array}{l}N{=\!=}N\\ C(OH){:}CH\end{array}$, or on 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid, a compound is formed, which may be formulated either as 4-*nitroso*-5-*hydroxy*-1-*phenyltriazole*,  $NPh<\begin{array}{l}N{=\!=}N\\ C(OH){:}C\cdot NO\end{array}$, or more probably as 4-iso*nitroso*-1-*phenyl*-5-*triazolone*,  $NPh<\begin{array}{l}N{=}N\\ CO\cdot C{:}N\cdot OH\end{array}$. It separates from a mixture of ether and light petroleum in silky, orange-coloured needles, which are completely decomposed at 195°; its *ammonium* salt forms violet plates.

4-*iso*Nitroso-1-phenyl-5-triazolone is of interest on account of the ease with which the ring is broken. When treated with concentrated hydrochloric acid, nitrogen is evolved, and *oxanilhydroxamic chloride*, NHPh·CO·CCl:N·OH, formed; this separates from a mixture of ether and light petroleum in colourless needles and begins to decompose at about 160°.

Oxanilhydroxamic anilide, NHPh·CO·C·NHPh:N·OH, obtained from the preceding chloride and aniline, separates from alcohol in colourless needles, m. p. 180°. Its constitution is established by its conversion into oxanilide and hydroxylamine by the action of fuming hydrochloric acid.

Oxanilhydroxamic acid, NHPh·CO·C(OH):N·OH, obtained by the action of water on oxanilhydroxamic chloride, separates from alcohol in colourless needles and decomposes at 163°. When heated in a vacuum at a high temperature, it forms diphenylcarbamide, carbon dioxide, and ammonia.

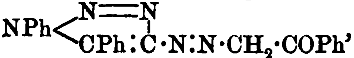
When 4-*iso*nitroso-1-phenyl-5-triazolone is boiled with water, in addition to oxanilhydroxamic acid two colourless, crystalline isomerides, $C_{16}H_{12}O_4N_4$, are formed according to the equation $2C_8H_8O_3N_2 = C_{16}H_{12}O_4N_4 + 2H_2O$. The constitution of these compounds has not yet been absolutely settled. The one is probably *glyoximeperoxidedicarboxylanilide*,  $\begin{array}{l}\mathrm{NHPh{\cdot}CO{\cdot}C{:}N{\cdot}O} \\ \mathrm{NHPh{\cdot}CO{\cdot}C{:}N{\cdot}O}\end{array}$, which may be obtained either by boiling 4-*iso*nitroso-1-phenyl-5-triazolone with dilute sulphuric acid or by boiling oxanilhydroxamic chloride with aqueous sodium acetate; it separates from alcohol in prisms, m. p. 187°; it is very stable towards oxidising agents, but is readily attacked by reducing agents. The second isomeride is probably 3 : 6-*dioximino*-2 : 5-*diketo*-1 : 4-*diphenylpiperazine*,  $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CO{\cdot}C(N{\cdot}OH)} \\ \mathrm{C(N{\cdot}OH){\cdot}CO}\end{array}{>}\mathrm{NPh}$; it is best obtained by warming 4-*iso*nitroso-1-phenyl-5-triazolone with alcohol. It forms glistening, colourless leaflets and decomposes at 195°. Its alcoholic solution gives a red coloration with ferric chloride. When acted on by dilute sodium hydroxide, it is converted into oxanilhydroxamic anilide.

A. McK.

Syntheses with Azoimides. VI. Condensation of Phenylazoimide with Ketones.

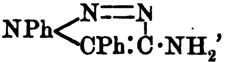
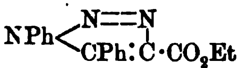
Otto Dimroth, Erich Frisoni, and Joseph Marshall (*Ber.*, **39**, 3920—3928. Compare Abstr., 1903, i, 127).—Since phenylazoimide readily interacts with acid esters, β-ketonic esters, &c., in the presence of sodium ethoxide with the formation of 1 : 2 : 3-triazole, it was probable that ketones would undergo condensation in an analogous manner. The authors accordingly investigated the action of phenylazoimide on acetone and on dypnone.

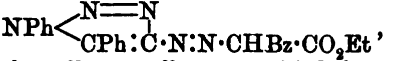
1 : 5-*Diphenyl*-1 : 2 : 3-*triazole*-4-*azoacetophenone*,



$$\mathrm{NPh}{<}\begin{array}{l}\mathrm{N{=\!=}N} \\ \mathrm{CPh{:}C{\cdot}N{:}N{\cdot}CH_2{\cdot}COPh}\end{array},$$

obtained by the interaction of acetophenone, phenylazoimide, and sodium ethoxide, separates from dilute alcohol in yellow leaflets, m. p. 176°. It is a weak acid and forms red salts; at the same time, as a triazole derivative, it exhibits basic character in so far as it forms a hydrochloride which is readily decomposed by water. The *sodium* salt is a brick-red powder; the *silver* salt is red; the *methyl* derivative forms colourless crystals, m. p. 133—135°; the *acetyl* derivative forms colourless crystals, m. p. 175°.

4-*Amino*-1 : 5-*diphenyl*-1 : 2 : 3-*triazole*,  $\mathrm{NPh}{<}\begin{array}{l}\mathrm{N{=\!=}N} \\ \mathrm{CPh{:}C{\cdot}NH_2}\end{array}$, obtained by the reduction of 1 : 5-diphenyl-1 : 2 : 3-triazole-4-azoacetophenone with zinc dust and ammonia in alcoholic suspension, forms colourless needles, m. p. 124°. Its constitution follows from its synthesis from ethyl 1 : 5-diphenyl-1 : 2 : 3-triazole-4-carboxylate,  $NPh<\begin{matrix}N{=}N\\ CPh{:}C\cdot CO_2Et\end{matrix}$ (Abstr., 1903, i, 127), which was first converted into its *hydrazide*, $C_{15}H_{13}ON_5$; this separates from water in colourless needles, m. p. 166—167°. The corresponding *azoimide*, m. p. 111—112°, when boiled with alcohol, forms the *urethane*, $C_{17}H_{16}O_2N_4$, from which 4-amino-1 : 5-diphenyl-1 : 2 : 3-triazole is readily obtained by boiling with concentrated hydrochloric acid. When the base is diazotised and then coupled with ethyl benzoylacetate, it forms the azo-compound, *ethyl* 1 : 5-*diphenyl*-1 : 2 : 3-*triazole*-4-*azobenzoylacetate*,

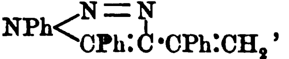


$$NPh<\begin{matrix}N{=}N\\ CPh{:}C\cdot N{:}N\cdot CHBz\cdot CO_2Et\end{matrix},$$

which crystallises in yellow needles, m. p. 148°, from which on boiling with alcoholic potassium hydroxide the carbethoxy-group is eliminated with the formation of a compound identical in all respects with that obtained by the interaction of phenylazoimide with acetophenone.

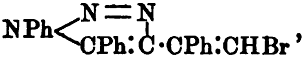
The mechanism of the formation of 1 : 5-diphenyl-1 : 2 : 3-triazole-4-azoacetophenone from phenylazoimide and acetophenone is discussed; it is assumed that the first phase of the action consists in the formation of a diazoamino-compound.

When phenylazoimide and dypnone are condensed in presence of sodium ethoxide, 1 : 5-*diphenyl*-4-α-*styryl*-1 : 2 : 3-*triazole*,

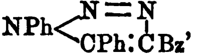


$$NPh<\begin{matrix}N{=}N\\ CPh{:}C\cdot CPh{:}CH_2\end{matrix},$$

is obtained; it forms yellow prisms, m. p. 127—128°. The action is represented by the equation $C_6H_5N_3 + C_{16}H_{14}O = C_{22}H_{17}N_3 + H_2O$. The compound is unsaturated, uniting with bromine to form the *dibromide*, $C_{22}H_{17}N_3Br_2$, which crystallises in colourless needles and melts and decomposes at 195°. When boiled with alcohol, hydrogen bromide is quantitatively eliminated, and the *monobromide*,

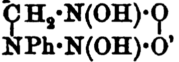


$$NPh<\begin{matrix}N{=}N\\ CPh{:}C\cdot CPh{:}CHBr\end{matrix},$$

obtained; the latter separates in colourless prisms, m. p. 112—113°. When oxidised by permanganate in the cold, 1 : 5-diphenyl-4-α-styryl-1 : 2 : 3-triazole forms 4-*benzoyl*-1 : 5-*diphenyl*-1 : 2 : 3-*triazole*,  $NPh<\begin{matrix}N{=}N\\ CPh{:}CBz\end{matrix}$, which separates from alcohol in spear-shaped crystals, m. p. 166°. The same compound may be formed by the condensation of phenylazoimide with dibenzoylmethane in the presence of sodium methoxide.

A. McK.

Compounds containing a previously Unknown Ring. II. Milorad Z. Jovitschitsch (*Ber.*, 1906, **39**, 3821—3830. Compare Abstr., 1898, i, 93; 1899, i, 239; 1902, i, 202).—After repeated recrystallisations from water, phenyldioxatriazine crystallises in light green needles, commences to decompose above 250°, and forms a gelatinous silver salt. When boiled with an excess of *N*/10 alkali hydroxide solution, phenyldioxatriazine or its ethyl carboxylate yields a deep red solution of the sodium derivative of phenyldihydroxydihydrodioxatriazine and not of phenyldioxatriazine as previously supposed. 3 : 6-*Dihydroxy*-4-*phenyldihydro*-1 : 2 : 3 : 4 : 6-*dioxatriazine*,



$\begin{array}{l}CH_2\cdot N(OH)\cdot O\\ NPh\cdot N(OH)\cdot O\end{array}$, crystallises in golden scales, m. p. 205°, and is moderately soluble in alcohol. The *monoalkali* salts become yellow on exposure to air; the *dialkali* salts are stable; the *silver* salt,

$$C_7H_7O_4N_3Ag_2,$$

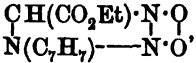
is reddish-brown.

The o-*toluidine* derivative of ethyl oximinoacetate,

$$C_7H_7\cdot NH\cdot C(NOH)\cdot COEt,$$

prepared in a quantitative yield by the action of 2 mols. of *o*-toluidine on ethyl chloro-oximinoacetate in ethereal solution, crystallises in white octahedra, m. p. 88°, the m-*toluidine* derivative, m. p. 123°, obtained in the same way, but in poorer yields, crystallises on dilution of its alcoholic solution. The p-*toluidine* derivative, m. p. 125°, crystallises on evaporation of its ethereal solution. The m-*xylidine* derivative, m. p. 79°, crystallises from dilute alcohol.

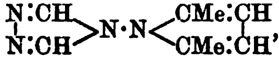
Ethyl 4-o-*tolyldioxatriazine*-5-*carboxylate*,



$\begin{array}{l}CH(CO_2Et)\cdot N\cdot O\\ N(C_7H_7)\text{——}N\cdot O\end{array}$, formed by the action of nitrous acid on the *o*-toluidine derivative of ethyl oximinoacetate in concentrated sulphuric acid, crystallises in silky, matted, voluminous needles, m. p. 157°, decomposes immediately above its melting point, and dissolves in aqueous alkali hydroxides, forming a violet *monoalkali* salt; the *silver* salt is red. 4-o-*Tolyldioxatriazine*, prepared by hydrolysis of the ethyl carboxylate with more than 2 mols. of *N*/10 alkali hydroxide, crystallises from hot water in light yellow needles, commences to blacken at 240°, m. p. 254°, forms a yellow, gelatinous *silver* salt, and when boiled with an acid yields a *substance* crystallising in white needles, m. p. 254°, and giving an intense yellow coloration with alkali hydroxides. 3 : 6-*Dihydroxy*-4-o-*tolyldihydrodioxatriazine*, formed by boiling the dioxatriazine or its ethyl carboxylate with an excess of *N*/10 alkali hydroxide, crystallises from hot water in slender, golden scales, m. p. 178°, forms *mono*- and *di-alkali* and a *silver* salt, and when boiled with acids yields the white substance, m. p. 254°. *Ethyl* 4-m-*tolyldioxatriazine*-5-*carboxylate* is formed in the same manner and has properties similar to those of the *o*-tolyl compound.

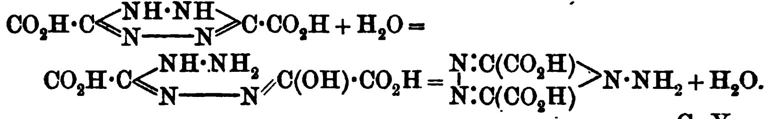
Ethyl 4-m-*xylyldioxatriazinecarboxylate* gives violet to red colorations with alkali hydroxides. G. Y.

"Dihydrotetrazine." Condensation of 1-Amino-1:3:4-triazole with Acetonylacetone. CARL BÜLOW (*Ber.*, 1906, **39**, 4106—4109. Compare Abstr., 1906, i, 905).—As ethyl 1-(1′)-triazole-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, like other pyrrole derivatives prepared by condensation of amines with ethyl diacetyl succinate, does not give the characteristic pyrrole reactions, the author has prepared 1-(4′)-*triazole*-2 : 5-*dimethylpyrrole*,



$\begin{array}{l}N\!:\!CH\\ N\!:\!CH\end{array}\!\!>\!N\cdot N\!<\!\!\begin{array}{l}CMe\!:\!CH\\ CMe\!:\!CH\end{array}$, by boiling 1-amino-1 : 2 : 4-triazole with acetonylacetone in acetic acid solution. This crystallises in long, stout needles, m. p. 151°, is readily soluble in organic solvents with the exception of light petroleum, and gives Laubenheimer's pyrrole reaction.

Curtius, Darapsky, and Müller's formula for bisdiazoacetic acid (this vol., i, 21) allows of a simple explanation of the conversion of this into 1-amino-1 : 3 : 4-triazole-2 : 5-dicarboxylic acid :



$$CO_2H\cdot C<{\substack{NH\cdot NH\\ N\text{——}N}}>C\cdot CO_2H + H_2O =$$

$$CO_2H\cdot C<{\substack{NH\cdot NH_2\\ N\text{———}N}}\diagup C(OH)\cdot CO_2H = {\substack{N:C(CO_2H)\\ N:C(CO_2H)}}>N\cdot NH_2 + H_2O.$$

G. Y.

Electrochemical Reduction of *o*-Nitroacetanilide. Kurt Brand and Edward Stohr (*Ber.*, 1906, **39**, 4058—4068. Compare Brand, Abstr., 1905, i, 770; Bamberger, Abstr., 1895, i, 217; Elbs, Abstr., 1901, i, 74; Willstätter and Pfannenstiel, Abstr., 1905, i, 723; Niementowski, Abstr., 1906, i, 319).—The electrochemical reduction of *o*-nitroacetanilide in a solution of sodium acetate in alcohol, water, and ethyl acetate, with a nickel wire gauze cathode and a current density of 2—3 amperes per square decimetre, in the cold, leads to the formation of *o*-azoacetanilide, in a 25 °/₀ yield, and traces of *o*-nitroaniline, *o*-phenylenediamine, and 2-methylbenziminazole. If a mercury cathode is employed, *o*-azoxyacetanilide also is obtained, but only in small quantity as it is readily reduced further to *o*-azoacetanilide.

The principal product of the reduction in mineral acid solution is *o*-phenylenediamine, whilst 2-methylbenziminazole is formed in concentrated acetic acid solution in presence of sodium acetate and stannous chloride.

On reduction in the manner previously described for nitrobenzene (Abstr., 1905, i, 770), but in a solution of sodium acetate in glacial acetic acid and alcohol, and with a current density of 5 amperes per square decimetre, *o*-nitroacetanilide yields *o*-azoxy- and *o*-azo-acetanilide and o-*hydroxylaminoacetanilide*, $NHAc\cdot C_6H_4\cdot NH\cdot OH$, which remains in solution, and reduces silver nitrate and Fehling's solutions; it changes gradually in neutral solution into *o*-azoacetanilide or more rapidly in alkaline solution, when *o*-azoxyacetanilide, 2-methylbenziminazole, and *o*-nitroaniline also are formed. Oxidation of *o*-hydroxylaminoacetanilide by means of silver nitrate, copper sulphate, or ferric chloride in sodium acetate solution, leads to the formation of o-*nitrosoacetanilide*, $NO\cdot C_6H_4\cdot NHAc$, which crystallises in stout needles or leaflets, m. p. 105—106°, and is converted into *o*-azoxyacetanilide when boiled with alcohol or treated with dilute acids or alkali hydroxides at the ordinary temperature.

o-Azoxyacetanilide, $ON_2(C_6H_4\cdot NHAc)_2$, is prepared by the action of sodium hydroxide on a molecular solution of *o*-nitrosoacetanilide and *o*-hydroxylaminoacetanilide in alcohol. It crystallises in brownish-orange-yellow leaflets or needles, m. p. 185°, and when boiled with moderately concentrated alcoholic hydrogen chloride, yields *o-azoxyaniline*, $C_{12}H_{12}ON_4$, which crystallises in red needles, m. p. 115°; the *hydrochloride*, $C_{12}H_{12}ON_4,2HCl$, forms greyish-yellow leaflets, m. p. 220°, decomposing. The base yields *o*-azoxybenzanilide when benzoylated in pyridine solution.

The action of formaldehyde on *o*-hydroxylaminoacetanilide in neutral solution leads to the formation of the *condensation* product, $CH_2(O\cdot NH\cdot C_6H_4\cdot NHAc)_2$, which is obtained in yellow needles, m. p. 144°, decomposing, is insoluble in almost all organic solvents, and when boiled with alcohol or dilute acids or alkali hydroxides, decomposes to formaldehyde and *o*-azoxyacetanilide.

Benzylidene-o-aminoacetanilide, $CHPh:N\cdot C_6H_4\cdot NHAc$, is formed by reduction of *o*-nitroacetanilide in the same manner as described above for the preparation of *o*-hydroxylaminoacetanilide but with a current density of 10 amperes per square decimetre, and addition of benzaldehyde to the reduced solution. It crystallises in glistening, golden-yellow leaflets, m. p. 125°, forms benzaldehyde on prolonged boiling with water, and yields 2-methylbenziminazole and benzaldehyde when heated with dilute acids. G. Y.

Change of Colour in Constitutively Unchangeable Substances. ARTHUR HANTZSCH and W. H. GLOVER (*Ber.*, 1906, **39**, 4153—4174).—Solutions of "neutral" substances such as azo-compounds, quinones, and diketones have been examined by green light in Martens and Grünbaum's improved form of König's spectrophotometer. In accordance with Beer's law, the colour intensity is proportional to the concentration. The colour of any one substance depends very largely on the nature of the solvent, those containing oxygen forming solutions of a lighter shade, probably containing a loose molecular compound of solvent and solute. The alkali salts of hydroxyazo-compounds and of quinonedioximes are more intensely coloured than the parent substances; the same is true of the alkyl and acyl derivatives of benzeneazophenol and of tolueneazophenol (compare Kauffmann, Abstr., 1906, i, 577), the colour intensity being independent of the nature of the substituent but proportional to the molecular weight. Of the derivatives of β-naphthaquinonedioxime, the alkyl and acyl compounds are the least coloured, and the alkali salts most intensely coloured.

The new compounds described are: p-*benzeneazophenyl benzyl ether*, $PhN_2\cdot C_6H_4\cdot O\cdot CH_2Ph$, yellow needles, m. p. 116°; *tolueneazophenyl benzoate*, $C_7H_7\cdot N_2\cdot C_6H_4\cdot OBz$, orange-red prisms, m. p. 158°; various metallic *salts* of *o*-benzoquinonedioxime; *benzyloxyaminotribromo-o-benzoquinone*, $C_7H_7\cdot O\cdot NH\cdot C_6Br_3O_2$, orange-yellow needles, m. p. 170°, decomposing; the *benzoyl* derivative of β-naphthaquinonedioxime α-methyl ether, $OMe\cdot N:C_{10}H_6:NOBz$, faintly yellow leaflets, m. p. 119°; *β-naphthaquinonemonoxime benzyl ether*, $O:C_{10}H_6:N\cdot OC_7H_7$, golden-yellow prisms, m. p. 101°; *β-naphthaquinonedioxime benzyl ether*, $NOH:C_{10}H_6:N\cdot OC_7H_7$, yellow prisms, m. p. 168°, and its *benzoyl* derivative, $NOBz:C_{10}H_6:N\cdot OC_7H_7$, faintly yellow needles, m. p. 116°.
C. S.

Behaviour of Certain Artificial Dyes with Liquid Sulphur Dioxide. EUGÈNE GRANDMOUGIN (*Zeit. Farb. Ind.*, 1906, **5**, 383—385).—The colours produced by dissolving azo-dyes in liquid sulphur dioxide are comparable with those given by the same dyes when dissolved in acetic acid, and different from the colours obtained with concentrated sulphuric acid. It appears that salt formation does not occur and that the liquid sulphur dioxides acts merely as a solvent. The substances examined were: azobenzene, hydroxyazobenzene, aminoazobenzene, benzeneazo-β-naphthol, 1 : 2- and 1 : 4-benzeneazo-α-naphthols, benzeneazo-salicylic acid, benzeneazo-α-hydroxynaphthoic acid, and benzenedisazo-α-naphthol.

Several of these can be recrystallised from liquid sulphur dioxide.

W. A. D.

The Chemical Functions of Textile Fibres. Léo Vignon (*Compt. rend.*, 1906, **143**, 550—552).—The author has shown previously (Abstr., 1890, 553, 939; *Compt. rend.*, 1898, **127**, 872) that from a chemical point of view fabrics of animal origin are to be considered as amino-acids, and those of vegetable origin as alcohols; the present paper contains an account of experiments made on wool, silk, and cotton to determine the partition coefficient of an acid, base, or salt between the fabric and water. The experiments were conducted by immersing skeins of known weight for one hour at the ordinary temperature in 1 or 0·1 per cent. solutions of acids, bases, or salts, and determining the amount of acid, base, or salt in the bath both before and after the experiment. Control experiments were also made in which the fabric was replaced by pure pulverised wood charcoal. The results confirm the conclusions of the earlier experiments, and show further that the acidic or basic functions of the textile fibre increase with the dilution of the aqueous solution of the base or acid, and that porous substances such as charcoal are chemically inert.

M. A. W.

Heat Production and Enzyme Action. I. General. Franz Tangl (*Pflüger's Archiv*, 1906, **114**, 1—6). **II. Action of Pepsin.** Roland von Lengyel (*ibid.*, 7—10). **III. Action of Trypsin.** Paul Hári (*ibid.*, 11—51).—In the enzyme actions investigated, there is no change of potential into other forms of energy and no apparent development of heat.

W. D. H.

Catalases. Amedeo Herlitzka (*Atti. R. Accad. Lincei*, 1906, [v], **15**, ii, 333—341).—The action of catalases on hydrogen peroxide is not a unimolecular reaction, and further, as the partial pressure or concentration of the oxygen has no influence on the action of catalases, the action is not a reversible one.

In presence of small quantities of manganese lactate, hydrogen peroxide prevents the oxidation of guaiacum resin. This apparently paradoxical behaviour is explained according to the views of Bertrand (compare Abstr., 1897, ii, 493; 1898, i, 53), who showed that, the weaker the acid of a manganese salt the greater is the oxidising action of the salt. Further, the weaker the acid, the greater will be the amount of hydrolysis of the manganese salt and hence the greater the concentration of the oxide of manganese formed. But the increased ionising action of hydrogen peroxide over that of water causes considerable dissociation of even weak acids, so that the hydrolysis of the manganese salt and the formation of oxide of manganese become very limited. If, however, catalase is added, the hydrogen peroxide is destroyed and the guaiacum resin consequently oxidised. T. H. P.

Studies on Enzyme Action. Lipase II. Henry E. Armstrong and Ernest Ormerod (*Proc. Roy. Soc.*, 1906, B., 78, 376—385. Compare Abstr., 1906, i, 126).—Experiments made in the hope of discovering an explanation of the selective power displayed by the enzyme, which by preference promotes the hydrolysis of esters of the higher fatty acids, such as occur in natural fats. *Ricinus* lipase alone has very little or no effect on ethyl butyrate. In presence of $N/5$ acetic acid, the butyrate is slowly hydrolysed. The extent of hydrolysis depends both on the amount of enzyme and to a certain point on the proportion of acid present. In the case of natural fats the liberated acids are too feeble and too insoluble materially to affect the process. Glycerol only retards hydrolysis when more than 25 per cent. is present; and the retarding effect of alcohol is approximately proportional to the amount.

Since the ethereal salts hydrolysed under the influence of lipase are all of the type $R'\cdot CO\cdot OX'$, and both R' and X' may be varied within wide limits, it follows that the carboxyl group is the controlling influence. It is suggested that the association of the enzyme with carboxyl may be prevented by hydration, so that salts which are the more attractive of water will be the less readily hydrolysed. This would accord with the fact that the higher members of the acetic acid series are more readily hydrolysed by lipase (although not by ordinary hydrolytic agents) than the lower members which tend to form hydrates (hydrols) such as $OEt\cdot CMe(OH)_2$; and the hypothesis is also strikingly supported by comparative results obtained with ethylic malonate, succinate, malate, and tartrate.

Animal lipase seems to differ from vegetable lipase only in being less active, the superiority of the seed residue being perhaps due to its much greater emulsifying power.

It is important, especially when employing animal lipase, that the esters to be compared should be in solution.

N. H. J. M.

Hydrolytic Action of the Maltase of Malt. Luigi Marino and G. Fiorentino (*Gazzetta*, 1906, 36, ii, 395—427).—The maltase of malt decomposes maltose and also those natural and artificial glucosides which are decomposed by emulsin. Of the artificial glucosides, maltase of malt only attacks the β-compounds of dextrose; it is hence supposed that those natural glucosides which are acted on by maltase are also β-derivatives of dextrose. The results indicate that one enzyme alone can produce hydrolysis in cases in which recourse was formerly had to the action of two or more enzymes, and indicate also the general applicability of Fischer's law concerning the relations between the configuration and the action of enzymes. Maltase obtained by the method of Marino and Sericano (Abstr., 1906, i, 125) contains no emulsin, since, when a concentrated solution of it acts on amygdalin, the hydrogen cyanide liberated renders the maltase almost inactive, and, if the enzyme is recovered, it is found to have only an extremely slight action on maltose or salicin; under identical conditions, the addition of a trace of emulsin to the recovered enzyme leads to the decomposition of at least 75 per cent. of the salicin taken.

Maltase obtained from malt, like that of beer yeast, is able to act synthetically, yielding *iso*maltose, so that it is probable that, if the two maltases were purified, they would be found to be identical.

Benzaldehyde and hydrocyanic acid have no influence on the activity of emulsin. T. H. P.

Alcoholic Ferment of Yeast-juice. Part II. Co-ferment of Yeast-juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1906, B, **78**, 369—375. Compare Abstr., 1906, i, 470).—The residue obtained by filtering yeast-juice though a Martin gelatin filter can be completely freed from the co-ferment by redissolving in water and filtering; it is then dried for fifteen hours over sulphuric acid in a vacuum. The inactive residue loses its potential activity slowly; after two months the rate of fermentation in presence of boiled yeast-juice was about one-third of that attained with the freshly prepared residue.

Cessation of fermentation in a mixture of the inactive residue and co-ferment may be due to the disappearance of either the one or the other, according to the relative amounts originally present. In absence of dextrose, the co-ferment usually disappears in about forty-eight hours (at 26°); in presence of 10 per cent. of dextrose a small amount of co-ferment remained at the end of four days.

Whilst, as previously shown, soluble phosphates exert a remarkable effect on the fermentation of dextrose by yeast-juice, their addition to a solution of the inactive residue in dextrose does not set up fermentation. N. H. J. M.

Comparative Investigations of Vegetable Proteolytic Ferments. EMIL ABDERHALDEN and YUTAKA TERUUCHI (*Zeit. physiol. Chem.*, 1906, **49**, 21—25).—Yeast-juice splits glycylglycine and glycyl-*l*-tyrosine. The latter peptide lends itself very well to such experiments because it is readily soluble in water; it is also split by papain, but not by the fluid from the pitchers of *Nepenthes*. W. D. H.

The Action of Proteolytic Ferments of Germinating Seeds of Wheat and Lupins on Polypeptides. EMIL ABDERHALDEN and ALFRED SCHITTENHELM (*Zeit. physiol. Chem.*, 1906, **49**, 26—30).—The juices expressed from the germinating seeds of wheat and lupin seeds split *dl*-leucylglycine, glycylglycine, and dialanylcystine. In no case was an amino-group eliminated. W. D. H.

Organic Chemistry.

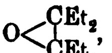
Melting Points of Hydrocarbons Homologous with Methane. D. E. Tsakalotos (*Compt. rend.*, 1906, **143**, 1235—1236).—When the boiling points of the members of a homologous series are plotted against the number of carbon atoms the curve thus obtained is smooth (Young, Abstr., 1905, ii, 231), but the m. p. curve, similarly constructed, shows a number of zigzags (maxima and minima), and in the case of the hydrocarbons of the methane series the curve is irregular from C_9H_{20} to $C_{15}H_{32}$, and then becomes regular up to $C_{60}H_{122}$. The melting points of the hydrocarbons between the limits $C_{16}H_{34}$ and $C_{60}H_{122}$ can be calculated from the formula $\Delta n = [85 - 0{\cdot}01882(n-1)^2]/(n-1)$, where Δn is the difference between the m. p. of one hydrocarbon of the series and that of its next higher homologue and n is the number of carbon atoms in the molecule. In the original are tabulated the experimental and calculated values of the known hydrocarbons of the methane series between the values $n = 16$ and $n = 60$, and with the exception of the hydrocarbon $C_{35}H_{72}$, there is a very close agreement between the two sets of values. M. A. W.

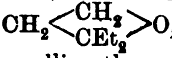
Preservation of Chloroform. Pierre Breteau and Paul Woog (*Compt. rend.*, 1906, **143**, 1193—1195).—Chloroform exposed to air and light decomposes into hydrogen chloride and phosgene; and the latter is very toxic. It is essential for the surgeon that chloroform should be pure, and impurities of the kind indicated are best detected by congo-red, which is turned blue. This succeeds when silver nitrate gives no trace of precipitate. W. D. H.

Conversion of Conine into Dichloro- and Dibromo-Octanes. Julius von Braun and E. Schmitz (*Ber.*, 1906, **39**, 4365—4369).—The action of phosphorus penta-chloride or -bromide on benzoylconine leads to the formation of *dichloro-octane*, b. p. 105—107°/16 mm. and of *dibromo-octane*, b. p. 123—129°/11 mm. respectively, which should have, from their method of formation, the composition

$$CH_2X{\cdot}[CH_2]_3{\cdot}CHXPr^{\alpha}.$$

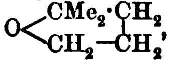
Conine derivatives cannot be re-formed from these substances; only one-half of the halogen is displaced by the action of benzylamine or of potassium cyanide. C. S.

Synthesis of Halogenated *tert*.-Alcohols by Means of Organo-magnesium Compounds. Mdlle. R. Dalebroux and Henri Wuyts (*Bull. Soc. chim., Belg.*, 1906, **20**, 156—158. Compare Henry, Abstr., 1906, i, 133, and Süsskind, *ibid.*).—Ethyl chloroacetate (1 mol.) reacts with magnesium ethyl bromide (3 mols.), in presence of ether, to form a complex, which on treatment with water furnishes *chloromethyldiethylcarbinol*, $CH_2Cl{\cdot}CEt_2{\cdot}OH$, a slightly viscous liquid, b. p. 70°/20 mm., D_4^{15} 1·0267. When distilled with a slight excess of potassium hydroxide it yields *aa-diethylethylene oxide*,  $O<\begin{matrix}CEt_2\\ |\\ CEt_2\end{matrix}$, a mobile liquid with a slight odour of mint, b. p. 107°, D_4^{15} 0·8403.

Ethyl β-iodopropionate reacts similarly with magnesium ethyl bromide, forming *γ-iodo-aa-diethylpropyl alcohol*, $CH_2I{\cdot}CH_2{\cdot}CEt_2{\cdot}OH$, a slightly viscous liquid with a characteristic odour. This on distillation over potassium hydroxide yields *aa-diethylpropylene oxide*,  $CH_2<\begin{matrix}CH_2\\ CEt_2\end{matrix}>O$, a colourless, mobile liquid with an odour simultaneously recalling those of anise and of mint; b. p. 126—130°. T. A. H.

Butyrolactone and *as*-Dimethylsuccinic Glycol [δ-Methylpentane-αδ-diol]. LOUIS HENRY (*Compt. rend.*, 1906, **143**, 1221—1225. Compare Houben, Abstr., 1904, i, 334).—Butyrolactone (Abstr., 1886, 216) reacts with magnesium methyl iodide in the presence of dry ether to form *δ methylpentane-αδ-diol*,

$$OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

which is a viscous, colourless, odourless liquid with a bitter-sweet taste, b. p. 158°/65 mm. or 222°/774 mm. (corr.). It contains both the tertiary and primary alcoholic groupings, and reacts (1) with acetyl chloride to form the *chloroacetin*, $CMe_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$ (*δ-chloro-δ-methylpentyl acetate*), a colourless, mobile liquid with a disagreeable odour, b. p. 132°/70 mm. or 190°/747 mm. with evolution of hydrogen chloride; and (2) with dilute sulphuric acid (15%) to form its *oxide* (*2 : 2-dimethyltetrahydrofuran*),  $O<\begin{matrix}CMe_2{\cdot}CH_2\\ |\\ CH_2{-}CH_2\end{matrix}$, a colourless, mobile liquid, b. p. 95°/756 mm.

Ethyl γ-chlorobutyrate, $CH_2Cl{\cdot}CH_2.CH_2{\cdot}CO_2Et$, yields with magnesium methyl bromide the *chlorohydrin* (*α-chloro-δ-methylpentane-δ-ol*), $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl$, which decomposes on heating into 2 : 2-dimethyltetrahydrofuran and *α-chloro-δ-methyl-Δ^γ-amylene*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2Cl,$$

b. p. 135°; and is converted by the action of fuming hydrochloric acid or acetyl chloride into the *dichlorohydrin* (*αδ-dichloro-δ-methylpentane*), $CMe_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl$, b. p. 179—180°, which does not solidify at −80°. M. A. W.

Influence of Radicles on the Character of the Residual Valencies of Oxygen. WLADIMIR TSCHELINZEFF (*Compt. rend.*, 1906, **143**, 1237—1239. Compare Abstr., 1905, ii, 802; 1906, ii, 334; Blaise, Abstr., 1901, i, 317).—The author has measured the thermal effects q and q' corresponding with the combination of an alkyl magnesium iodide with two successive molecular proportions of an

	q.	q'.	Q.	$Q=q+q'$.
OEt_2	6·63	6·16	12·60	12·79
$EtO{\cdot}C_3H_7$	6·15	5·93	12·12	12·08
$EtO{\cdot}C_4H_9$(*iso*)	5·84	5·37	11·40	11·21
$EtO{\cdot}C_5H_{11}$(*iso*)	6·17	5·47	11·73	11·64
$O(C_5H_{11})_2$(*iso*)	5·91	4·54	10·31	10·45
PhOMe	—	—	—	—
PhOEt	—	—	—	—

ether, also the value *Q* of its direct combination with 2 mols. of the ether; the alkyl magnesium iodide employed was $C_3H_7\cdot MgI$, and the results are tabulated on p. 106.

These figures show that in the aliphatic ethers the replacement of one radicle by another (with the exception of the *iso*amyl group) has very little effect on the character of the residual valencies of the oxygen atoms; but in the case of the aromatic radicles the nature of the reaction is quite different, there being practically no thermal effect accompanying the addition of one phenyl group. M. A. W.

Complex Ether-Oxides. MARCEL SOMMELET (*Ann. Chim. Phys.*, 1906, [viii], 9, 481—576).—A detailed account of the preparation and properties of the α-glycol ethers of the types $OH\cdot CR_2\cdot CH_2\cdot OX$ and $OH\cdot CRR'\cdot CH_2\cdot OX$, and of β-glycerol ethers of the type

$$OH\cdot CR(CH_2\cdot OX)_2,$$

and of the aldehydes of the respective types $CR_2H\cdot CHO$, $CRR'H\cdot CHO$, and $CH_2\colon CR\cdot CHO$ derived from them. Certain of these compounds have already been described in two earlier papers (Behal and Sommelet, Abstr., 1904, i, 222; and Sommelet, this vol., i, 21), and will therefore only be referred to in this present abstract in the cases where their physical constants have been amended or extended.

Alkyl esters of ethoxyacetic acid are readily prepared by the action of the corresponding alcohol on ethoxyacetic acid in the presence of hydrochloric acid; iso*butyl ethoxyacetate*, $OEt\cdot CH_2\cdot CO_2C_4H_9$, b. p. 186°/755 mm. (corr.); iso*amyl ethoxyacetate*, $OEt\cdot CH_2\cdot CO_2C_5H_{11}$, b. p. 204—205°/756 mm.; *benzyl ethoxyacetate*,

$$OEt\cdot CH_2\cdot CO_2CH_2Ph,$$

b. p. 155°/21 mm.; *phenyl ethoxyacetate*, obtained by the action of phenol on ethoxyacetyl chloride in pyridine solution, b. p. 139°/18 mm.; *ethoxyacetic anhydride*, $(OEt\cdot CH_2\cdot CO)_2O$, b. p. 142—143°/125 mm.

Ethoxyacetylacetone, $OEt\cdot CH_2\cdot CO\cdot CH_2\cdot COMe$, prepared from acetone and ethyl ethoxyacetate by the Claisen condensation, is a colourless oil, b. p. 83—84°/13 mm.; its *copper* derivative forms blue needles, m. p. 149°. *Ethoxyacetylmethylacetone*, $OEt\cdot CH_2\cdot CO\cdot CHMe\cdot COMe$, prepared by the action of methyl iodide on the sodium derivative of ethoxyacetylacetone in sealed tubes at 125°, is a pale yellow liquid, b. p. 103—105°/15 mm.; *ethoxyacetylethylacetone*, b. p. 116°/15 mm.

Of the ketones of the type $R\cdot CO\cdot CH_2\cdot OEt$ (Abstr., 1904, i, 222), prepared by the action of organomagnesium compounds on the corresponding cyanoalkyloxymethanes (this vol., i, 21), the densities and amended boiling points are given, and the semicarbazones described. *Ethoxyacetone-semicarbazone*, $OEt\cdot CH_2\cdot CMe\colon N\cdot NH\cdot CO\cdot NH_2$, forms prismatic needles, m. p. 96° (compare Leonardi and Franchis, Abstr., 1903, i, 788). α-Ethoxybutanone, b. p. 55°/24 mm. or 62·5°/33 mm.; D^{16}_4 0·914; the *semicarbazone*, m. p. 87°. α-Ethoxypentanone, b. p. 60°/11 mm. or 64—65°/17 mm., D^{16}_4 0·9218; the *semicarbazone*, m. p. 87°. *α-Ethoxy-δ-methylpentanone*, b. p. 67·5—68·5°/14 mm. or 73—74°/20 mm. and D^{16}_4 0·8912; the *semicarbazone*, m. p. 119°. α-Ethoxy-ε-methylhexanone, b. p. 88°/13 mm.; the *semicarbazone*, m. p. 89°. ω-Ethoxyacetophenone *oxime*, $OEt\cdot CH_2Ph\overset{\rangle}{:}NOH$, crystallises from ether or petroleum in prisms, m. p. 55°; the *semicarbazone*, m. p. 128°.

The densities of the α-glycol ethers, $OH\cdot CR_2\cdot CH_2\cdot OX$, already described (Abstr., 1904, i, 222), are as follows: $OH\cdot CMe_2\cdot CH_2\cdot OEt$, D_4^{15} 0·8786; $OH\cdot CEt_2\cdot CH_2\cdot OEt$, D_4^{15} 0·8961; $OH\cdot C(C_3H_7)_2\cdot CH_2\cdot OEt$, D_4^{19} 0·8716; $OH\cdot C(C_5H_{11})_2\cdot CH_2\cdot OEt$, D_4^{15} 0·8595; $OH\cdot CPh_2\cdot CH_2\cdot OEt$, D_4^{19} 1·094.

In addition to the α-glycol ethers of the type $OH\cdot CRR'\cdot CH_2\cdot OX$ previously mentioned (Abstr., 1904, i, 222), the following are described: *α-ethoxy-β-methylbutane-β-ol*, $OEt\cdot CH_2\cdot CMe(OH)\cdot C_2H_5$, b. p. 148—149°/763 mm., $D_4^{16\cdot5}$ 0·8825; *α-ethoxy-β-methylpentane-β-ol*, $OEt\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot Et$, b. p. 167—168°, $D_4^{16\cdot5}$ 0·8767; α-ethoxy-β-ethylpentane-β-ol, b. p. 182—183° or 77°/13—14 mm., and not 180—184° as previously stated, $D_4^{16\cdot5}$ 0·8786; *α-ethoxy-δ-methyl-β-ethylpentane-β-ol*, $OEt\cdot CH_2\cdot CEt(OH)\cdot CH_2Pr^{\beta}$, b. p. 97°/26 mm. or 93°/22 mm., $D_4^{16\cdot5}$ 0·8731; α-ethoxy-β-methyloctane-β-ol, b. p. 102—105°/11—12 mm., $D_4^{16\cdot5}$ 0·8665; α-ethoxy-β-methylnonane-β-ol, b. p. 118—119°/11 mm., $D_4^{16\cdot5}$ 0·8685; *α-ethoxy-β-methylundecane-β-ol*, $OEt\cdot CH_2\cdot CMe(OH)\cdot C_9H_{19}$, b. p. 152—153°/19 mm., $D_4^{16\cdot5}$ 0·8623.

β-Glycerol ethers of the type $OH\cdot CR(CH_2\cdot OX)_2$ are prepared by the condensation of the ethereal salt of the corresponding acid and the chloromethyl alkyl ether in the presence of magnesium and a little mercuric chloride. *β-Ethylglycerol αγ-diethyl ether*,

$$OH\cdot CEt(CH_2\cdot OEt)_2,$$

b. p. 84—86°/20 mm. or 195°/765 mm. (corr.), $D_4^{16\cdot5}$ 0·9503. *β-Propylglycerol αγ-diethyl ether*, $OH\cdot CPr^{\alpha}(CH_2\cdot OEt)_2$, b. p. 97°/16 mm. or 210°/760 mm, $D_4^{16\cdot5}$ 0·9195. *β-*iso*Butylglycerol αγ-diethyl ether*, $C_4H_9\cdot C(CH_2\cdot OEt)_2\cdot OH$, b. p. 111—112°/23 mm. or 215°/760 mm., $D_4^{16\cdot5}$ 0·9077. *β-*iso*Butylglycerol αγ-dipropyl ether*, $C_4H_9\cdot C(CH_2\cdot O\cdot C_8H_7)_2\cdot OH$, b. p. 139—140°/22—23 mm., $D_4^{16\cdot5}$ 0·8938. *β-*iso*Butylglycerol αγ-diisobutyl ether*, $C_4H_9\cdot C(CH_2\cdot O\cdot C_4H_9)_2\cdot OH$, b. p. 145—147°/18 mm., $D_4^{16\cdot5}$ 0·8766. *β-*iso*Butylglycerol αγ-diisoamyl ether*, $C_4H_9\cdot C(CH_2\cdot O\cdot C_5H_{11})_2\cdot OH$, b. p. 162°/12 mm. or 178°/25 mm., $D_4^{16\cdot5}$ 0·8785. *β-*n*-Amylglycerol αγ-diethyl ether*, $C_5H_{11}\cdot C(CH_2\cdot OEt)_2\cdot OH$, b. p. 118—119°/13 mm., $D_4^{16\cdot5}$ 0·9029. *β-Hexylglycerol αγ-diethyl ether*, $C_6H_{13}\cdot C(CH_2\cdot OEt)_2\cdot OH$, b. p. 135—136°/15 mm., $D_4^{16\cdot5}$ 0·9013. *β-Decenylglycerol αγ-diethyl ether*, $C_{10}H_{19}\cdot C(CH_2\cdot OEt)_2\cdot OH$, b. p. 180°/12 mm., $D_4^{16\cdot5}$ 0·9. *β-Octylglycerol αγ-diethyl ether*, $C_8H_{17}\cdot C(CH_2\cdot OEt)_2\cdot OH$, b. p. 160°/15 mm., $D_4^{16\cdot5}$ 0·8949. *β-Benzylglycerol αγ-diethyl ether*, $CH_2Ph\cdot C(CH_2\cdot OEt)_2\cdot OH$, b. p. 174°/14 mm., $D_4^{16\cdot5}$ 1·0091.

In addition to the aldehydes of the types $CR_2H\cdot CHO$ and $CRR'H\cdot CHO$ previously mentioned (Abstr., 1904, i, 222), certain of their derivatives and some new members of the series are described. α-Ethylbutaldehyde *oxime*, has b. p. 95°/34 mm., and the *semicarbazone*, m. p. 93—94°. α-Propylvaleraldehyde has D_4^{15} 0·8347, the *oxime*, b. p. 126°/47 mm., and the *semicarbazone*, m. p. 100—101°. α-*iso*Amyl*iso*heptaldehyde has D_4^{15} 0·8261, the *oxime* b. p. 153°/29 mm. *α-Ethyl*iso*hexaldehyde*, $C_4H_9\cdot CHEt\cdot CHO$, b. p. 154—155°; the *semicarbazone*, m. p. 97—98·5°. *α-Methyloctaldehyde*, $C_6H_8\cdot CHMe\cdot CHO$, b. p. 82—83°/20 mm.; the *semicarbazone*, m. p. 78—80°.

The following α-alkylacraldehydes were obtained by the action of anhydrous oxalic or pure (crystallisable) formic acid on the corresponding β-alkylglycerol αγ-dialkyl ethers.

α-*Ethylacraldehyde*, $CH_2{:}CEt{\cdot}CHO$, yields a crystalline *semicarbazone*, m. p. 192·5°. α-*Propylacraldehyde*, $CH_2{:}CPr^{\alpha}{\cdot}CHO$, b. p. 116—118°; the *semicarbazone*, m. p. 182°. α-iso*Butylacraldehyde*,

$$CH_2{:}C(C_4H_9){\cdot}CHO,$$

b. p. 133°, forms the semicarbazone, m. p. 184°, and yields *iso*butylacrylic acid, b. p. 118—120°/26 mm., on oxidation with silver oxide. α-*Amylacraldehyde*, $CH_2{:}C(C_5H_{11}){\cdot}CHO$, b. p. 59°/13 mm.; the *semicarbazone*, m. p. 154·5°. α-*Hexylacraldehyde*, $CH_2{:}C(C_6H_{18}){\cdot}CHO$, b. p. 78°/15 mm., yields the *semicarbazone*, m. p. 156°, and a crystalline *compound* with sodium hydrogen sulphite. α-*Octylacraldehyde*,

$$CH_2{:}C(C_8H_{17}){\cdot}CHO,$$

b. p. 104·5—106°/14 mm., and the semicarbazone m. p. 147·5°. α-*Benzylacraldehyde*, $CH_2{:}C(CH_2Ph){\cdot}CHO$, b. p. 118—120°/13 mm., and the semicarbazone, m. p. 189°. M. A. W.

Esterification of Arsenious Anhydride by Alcohols and Phenol. VICTOR AUGER (*Compt. rend.*, 1906, **143**, 907—909. Compare Abstr., 1902, i, 255).—Arsenious oxide is not volatile in steam, but is volatile in the vapour of methyl alcohol with the formation of methyl arsenite. Owing to the hydrolytic action of the water formed during the esterification the reaction is a balanced one, and the extent to which arsenious oxide is esterified by methyl alcohol and its homologues was determined by heating the alcohol with excess of crystalline arsenious oxide in a sealed tube at 160—180°, and estimating the arsenic in a portion of the cooled liquid by means of iodine, the difference between this quantity and the amount of arsenious oxide dissolved by the same quantity of alcohol in the cold representing approximately the amount of ester formed. In the case of methyl alcohol and arsenious oxide the equilibrium stage is reached in the cold in fourteen hours when 5·16% of ester is formed; after three hours at 150°, 6·5% of ester is formed, but after eighteen hours this has diminished to 5%. In the case of ethyl alcohol, 1·2% of ethyl arsenite is formed on heating, and the corresponding numbers for propyl, *iso*propyl, *iso*butyl, and *iso*amyl alcohols are 1·153, 0·112, 0·36, and 0·19 respectively.

It is possible to isolate the alkyl arsenites, either by fractional distillation in the case of *iso*butyl or *iso*amyl alcohol, or by removing the water from the alcohol and aqueous distillate by means of calcium carbide in the case of the other alcohols, and the following alkyl arsenites were thus formed: *propyl arsenite*, $As(OC_3H_7)_3$, b. p. 217°; n-*butyl arsenite*, $As(OC_4H_9)_3$, b. p. 263°; and iso*butyl arsenite*, $As(OC_4H_9)_3$, b. p. 242°.

Phenyl arsenite is formed when phenol is heated with excess of arsenious oxide. M. A. W.

Constitution of the Salts of Glucinum with the Fatty Acids, and the Valency of Glucinum. BORIS GLASMANN (*Chem. Zeit.*, 1907, **31**, 8—9).—According to Tanatar (Abstr., 1904, ii, 335) the composition of the volatile glucinum compounds described by Urbain and Lacombe (Abstr., 1902, i, 132) should be expressed by the formula Gl_2OR_6, in which glucinum is quadrivalent, and not by the formula Gl_4OR_6, in which this element is bivalent. The present author, however, regards these substances as salts of bivalent glucinum with anhydrides of ortho-fatty acids. It is assumed that acetic acid can act as an octo-basic acid by the elimination of 5 mols. of water from 6 mols. of ortho acid, $6CH_3{\cdot}C(OH)_3 = (CH_3C)_6O_5(OH)_8 + 5H_2O$, and the glucinum salt is regarded as a normal salt of this acid.

P. H.

ζ-Bromoheptoic Acid. JULIUS VON BRAUN (*Ber.*, 1906, **39**, 4362—4365).—*ζ-Phenoxyheptoic* acid, $OPh{\cdot}CH_2{\cdot}[CH_2]_5{\cdot}CO_2H$, m. p. 56—57°, is obtained quantitatively by hydrolysing the nitrile, prepared from ζ-phenoxyhexyl iodide; the *silver* salt is a white, crystalline powder decomposed only slowly by light. The acid and hydrobromic acid react at 80° to form ultimately ζ-bromoheptoic acid, $CH_2Br{\cdot}[CH_2]_5{\cdot}CO_2H$, m. p. 30—31°, b. p. 165—167°/12 mm., which distils almost unchanged between 280° and 300°, and by treatment with hot water yields a hydroxy-acid, which does not tend to form an eight-membered lactone ring (compare Baeyer and Villiger, Abstr., 1900, i, 328).

C. S.

Action of Reagents for the Aldehydic Function on Ethyl Glyoxalate. LOUIS J. SIMON and G. CHAVANNE (*Compt. rend.*, 1906, **143**, 904—907. Compare Abstr., 1906, i, 636).—Ethyl glyoxylate condenses with phenylhydrazine, hydroxylamine, or semicarbazide in the normal manner of compounds containing the aldehyde grouping, and the following compounds have been prepared. (1) The phenylhydrazone, $NHPh{\cdot}N{:}CH{\cdot}CO_2Et$, readily obtained by the action of phenylhydrazine hydrochloride on ethyl glyoxylate, forms pale yellow, triclinic crystals, m. p. 131°, can be distilled under reduced pressure at 170°, and is identical with the compound obtained by von Pechmann from diazobenzene acetate and ethyl sulphohydrazimethylenecarboxylate (Abstr., 1896, i, 678; compare also Reissert, Abstr., 1895, i, 460). The *potassium* salt, $N_2HPh{:}CH{\cdot}CO_2K,\frac{1}{2}C_2H_5{\cdot}OH$, is crystalline; the *acid*, $N_2HPh{:}CH{\cdot}CO_2H$, has m. p. 141° when heated slowly or 163° on a mercury bath (Reissert, Abstr., 1895, i, 460). (2) The oxime, $OH{\cdot}N{:}CH{\cdot}CO_2Et$, crystallises from ether and light petroleum in long, hard needles, m. p. 35°, b. p. 115°/15 mm. or 110—111°/12 mm., is identical with ethyl *iso*nitrosoacetate, obtained by Bouveault and Wahl by the action of nitrosylsulphuric acid on ethyl acetate (Abstr., 1904, i, 546), and on hydrolysis with dilute potassium carbonate yields the acid $OH{\cdot}N{:}CH{\cdot}CO_2H$, which decomposes at 130—140° according to the rate of heating (Bouveault and Wahl, *loc. cit.*); the amide, $(NOH){:}CH{\cdot}CO{\cdot}NH_2$, forms colourless, transparent, rhombic plates, which decompose at 126° (compare Ratz, Abstr., 1904, i, 857). (3) The *semicarbazone*, $NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}CO_2Et_2$, has m. p. 228° (decomp.); the acid decomposes at 258° on a mercury bath (Bouveault and Wahl give 240°, Abstr., 1904, i, 547). The *amide*,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CH{\cdot}CO{\cdot}NH_2,$$

forms a coarse, white mass decomposing at 217—218°. M. A. W.

Ricinoleic Acid. Adolf Grün (*Ber.*, 1906, **39**, 4400—4408. Compare Goldsobel, Abstr., 1895, i, 81; Walden, *ibid.*, i, 125; Behrend, *ibid.*, i, 647).—A study of the dihydroxystearic acids obtained from ricinoleic acid with a view to the elucidation of the relations existing between oleic, ricinoleic, and dihydroxystearic acids.

When ricinoleic acid is treated with sulphuric acid at −5° and the sulphuric esters hydrolysed, the product obtained consists of 12·6% of ricinoleic acid, 6·4% of dihydroxystearic acid, and 81% of the anhydro-compound $C_{17}H_{33}(OH)_2\cdot CO\cdot O\cdot C_{17}H_{33}(OH)\cdot CO_2H$, the latter being easily converted into the acid by alcoholic potash. Juillard's acid, m. p. 67—69° (Abstr., 1895, i, 82), is a mixture, and by repeated recrystallisation is resolved into four acids, one, m. p. 120°, only occurring in small quantities; the other three are dihydroxystearic acids. *Dihydroxystearic acid*, $C_{17}H_{33}(OH)_2\cdot CO_2H$, m. p. 108°, crystallises from alcohol in snow-white, crystalline aggregates, and is optically inactive. Between the other two acids there is a very close connexion as the d-θλ-*dihydroxystearic acid*,

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot[CH_2]_2\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H,$$

a white, crystalline powder, m. p. 90°, $[\alpha]_D$ +6·45° in alcohol, is converted into the d-l-*acid*, white, waxy, spherical, crystalline aggregates, m. p. 69·5°, optically inactive, in alcoholic solution spontaneously or on heating at 130—140°. The *diacetates* are bright yellow, mobile oils, that obtained from the *d*-acid giving α_D +10′ in 25% alcoholic solution. That the acid is an αδ-dihydroxy-derivative is shown by its conversion into a pyrrole derivative.

λ-*Bromo-θι-dihydroxystearic acid*,

$$CH_3\cdot[CH_2]_5\cdot CHBr\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H,$$

prepared by the action of phosphorus pentabromide on ricinoleic acid (compare Kasansky, Abstr., 1900, i, 426) and oxidation of the bromo-oleic acid so obtained by potassium permanganate, is a thick, pale yellow oil, which yields a solid benzoyl derivative. The bromine atom is firmly attached to the carbon, and attempts to reduce this compound to a dihydroxystearic acid failed. Reduction by zinc and hydrochloric acid of the iodo-derivative, obtained by digestion with calcium iodide at 100°, gave stearic acid. An attempt to reduce bromo-oleic acid was also unsuccessful. W. R.

Behaviour of Chloroform towards Methylene and Methenyl Groups. Arthur Kötz and W. Zörnig (*J. pr. Chem*, 1906, [ii], **74**, 425—448. Compare Oppenheim and Pfaff, this Journal, 1874, **27**, 1161; 1875, **28**, 1261. Conrad and Guthzeit, Abstr., 1883, 311. Claisen, Abstr., 1897, i, 592. Errera, Abstr., 1898, i, 298; 1901, i, 43; 1903, i, 265. Coutelle, Abstr., 1906, i, 139).—Acetylacetone, diketohydrindene, and malononitrile react with sodium ethoxide and chloroform in a similar manner to ethyl acetoacetate or ethyl malonate, whereas chloroform and sodium ethoxide do not react with benzyl cyanide or, below 100°, with deoxybenzoin; at higher temperatures, the last substance is reduced to stilbene.

In compounds containing two or three halogen atoms attached to the same carbon atom, the first and second halogen atoms may be substituted successively by the action of ethyl sodioalkylmalonates. The third halogen atom is exceedingly inactive, so that the halogen-free compounds, $CH[CR(CO_2Et)_2]_3$, cannot be formed by the action of chloroform on ethyl alkylmalonates, or of ethyl sodioalkylmalonates on ethyl chloromethylenebisalkylmalonates (compare Auwers and Keil, Abstr., 1903, i, 620). Only small amounts of the corresponding aldehydes have been obtained, and that with difficulty by the hydrolysis of the ethyl dichloromethylalkylmalonates.

The action of ethyl sodiomalonate on ethyl benzyldicarboxyglutaconate leads to the formation of only a small amount of ethyl benzylmalonate.

When treated with chloroform in absolute alcoholic solution, sodiomalononitrile yields *methenylbismalononitrilemonoimino-ethyl ether*, $C(CN)_2{:}CH\cdot CH(CN)\cdot C(OEt){:}NH,\frac{1}{2}H_2O$ or

$$CH(CN)_2\cdot CH{:}C(CN)\cdot C(OEt){:}NH,\tfrac{1}{2}H_2O,$$

which is precipitated by light petroleum from its solution in benzene in small, yellow crystals, m. p. 244° (decomp.).

Acetylacetone reacts with sodium ethoxide and chloroform in absolute alcoholic solution in a sealed tube at 130°, forming 5-hydroxy-2 : 4-diacetyltoluene (Claisen, *loc. cit.*).

The action of sodium ethoxide and chloroform on diketohydrindene in absolute alcoholic solution leads to the formation of methenylbisdiketohydrindene (Errera, Abstr., 1903, i, 265).

Ethyl iodomethylethylmalonate, $CH_2I\cdot CEt(CO_2Et)_2$, is formed by the action of an excess of methylene di-iodide on ethyl sodioethylmalonate in absolute ethereal solution; it is obtained as a colourless oil, b. p. 137—138°/12 mm., which gradually becomes red.

Ethyl methyldichloromethylmalonate, $CHCl_2\cdot CMe(CO_2Et)_2$, and *ethyl chloromethylenebismethylmalonate*, $CHCl[CMe(CO_2Et)_2]_2$, are formed together by the action of chloroform on ethyl sodiomethylmalonate and are separated by fractional distillation. The dichloro-ester is a transparent, white oil, b. p. 129°/12 mm., which yields small amounts of silver chloride when heated with silver oxide and water in a sealed tube at 100°. The monochloro-ester forms a yellow oil, b. p. 171—173° 12 mm.

In the same manner are formed *ethyl dichloromethylpropylmalonate*, $CHCl_2\cdot CPr(CO_2Et)_2$, b. p. 156—158°/16 mm.; *ethyl chloromethylenebispropylmalonate*, $CHCl[CPr(CO_2Et)_2]_2$, b. p. 210—213°/12 mm.; *ethyl dichloromethylbenzylmalonate*, $CHCl_2\cdot C(CO_2Et)_2\cdot CH_2Ph$, b. p. 207—209°/16 mm., and *ethyl chloromethylenebisbenzylmalonate*, $CHCl[C(COEt)_2\cdot CH_2Ph]_2$, b. p. 263—265°/14 mm.

The action of chloroform and sodium ethoxide on ethyl chloromalonate in absolute alcoholic solution at 120° leads to the formation of ethyl ethanetetracarboxylate. G. Y.

Condensation of Ethyl Oxalacetate and Ethylcyanoacetate in the presence of Piperidine. Ch. Schmitt (*Compt. rend.*, 1906, 143, 912—913. Compare Abstr., 1905, i, 508).—Ethyl oxalacetate condenses with ethyl cyanoacetate in the presence of piperidine to form *ethyl α-cyanopropylene-αβγ-tricarboxylate*,

$$CO_2Et\cdot CH_2\cdot C(CO_2Et){:}C(CN)\cdot CO_2Et,$$

which crystallises from benzene in needles, m. p. 75°, has a neutral reaction, and is isomeric with the acid compound obtained by Errera and Perciabosco by the action of dilute alkali on ethyl *iso*iminocarboxyaconitate (Abstr., 1902, i, 116), which probably has the constitution $CO_2Et\cdot CH(CN)\cdot C(CO_2Et)\colon CH(CO_2Et)$ (compare Rogerson and Thorpe, Trans., 1881, **39**, 631). Ethyl oxalacetate reacts with ethyl sodiocyanoacetate to form the *compound*,

$$CN\cdot CNa(CO_2Et)\cdot C(CO_2Et)\colon CH(CO_2Et,$$

which yields aconitic acid when treated with hydrochloric acid, ethyl 2 : 6-dihydroxypyridine-4 : 5-dicarboxylate (ethyl dihydroxycinchomeronate) when treated with cold concentrated sulphuric acid, and 2 : 6-dihydroxypyridine-4-carboxylic acid (citrazinic acid) on treatment with alcoholic potassium hydroxide. M. A. W.

Tetrabromo-derivative of Methyl Ethyl Ketone. PASTUREAU (*Compt. rend.*, 1906, **143**, 967—969. Compare Abstr., 1905, i, 572). —*Methyl ethyl ketone peroxide*, formed by the action of hydrogen peroxide on the ketone in dilute acid solution, reacts with bromine in presence of water at the ordinary temperature, yielding oxygen and the tetrabromo-derivative of the ketone. The reaction is completed on the water-bath.

Bromomethyl βββ-tribromoethyl ketone, $CH_2Br\cdot CO\cdot CH_2\cdot CBr_3$, crystallises from boiling 95% alcohol in white octahedra, m. p. 50°, has an irritating odour, and is insoluble in water. When boiled with aqueous potassium carbonate in a reflux apparatus, it yields acetol and acetic and formic acids. The formation of acetol must result from the decomposition of intermediately formed hydroxyacetoacetic acid, $OH\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H$. G. Y.

Compounds of Ketones with Ammonia. Methyl Propyl Ketone Ammonia. CARL THOMAE and HERMANN LEHR (*Arch. Pharm.*, 1906, **244**, 664).—*Methyl propyl ketone ammonia*, $C_{15}H_{30}N_2$ or $CMePr(N\colon CMePr)_2$, was obtained as an oil by the method already employed in the preparation of analogous compounds (Abstr., 1905, i, 509); the yield was 22% of the theoretical. C. F. B.

Physico-Chemical Investigations on Glycogen. FILIPPO BOTTAZZI and G. D'ERRICO (*Pflüger's Archiv*, 1906, **115**, 359—385).— The viscosity of glycogen solutions increases gradually with the concentration for dilute solutions, but as the solution becomes more concentrated the viscosity suddenly increases enormously with the concentration, thus pointing to some physical change in the nature of the solution. A curve is given showing the relationship between the viscosity and temperature for 10% and 20% solutions. No distinct breaks are noticeable.

The electrical conductivity of a solution of glycogen containing electrolytes first increases with the concentration, attains a maximum, then rapidly decreases, and, finally, slowly diminishes.

The melting point falls as the concentration increases, but the curve shows no characteristic breaks.

Saliva under suitable conditions reduces the viscosity of glycogen solutions, owing to its fermenting action on the carbohydrate. The effect is the most pronounced at the beginning of the diastatic action and in concentrated solutions. If the saliva is first boiled and the diastatic ferment destroyed, no appreciable effect on the viscosity is noticeable. J. J. S.

Novaine. FRIEDRICH KUTSCHER (*Zeit. physiol. Chem.*, 1906, **49**, 484. Compare this vol., i, 21).—When novaine is distilled with barium hydroxide the whole of the nitrogen is eliminated as trimethylamine. The residue contains a characteristic decomposition product which is probably crotonic acid. W. D. H.

Hydrogenation by Catalysis of Hexamethylenetetramine. GIUSEPPE GRASSI-CRISTALDI (*Gazzetta*, 1906, **36**, ii, 505—511).—Hexamethylenetetramine volatilises without decomposing, especially in a current of hydrogen, and sublimes on the cooler parts of the tube [S. DI FRANCO: the crystals formed are rhombic decahedra belonging to the regular system (compare Wohl, Abstr., 1886, 863)]. When a mixture of the base with reduced nickel is heated at 80° in a current of hydrogen, reduction takes place in the sense of the equation $N(CH_2{\cdot}N{:}CH_2)_3 + 9H_2 = NMe_3 + 3NH_3 + 3CH_4$. T. H. P.

Oxalylaminoacetic Acid: A Product of the Oxidation of Glycylglycine. ADOLF KRAEMER (*Ber.*, 1906, **39**, 4385—4388. Compare Pollak, Abstr., 1905, i, 750).—Pollak's statement that oxalylaminoacetic acid is formed when a cold aqueous solution of glycylglycine is oxidised by calcium permanganate is confirmed, as the calcium salt prepared by Pollak's method is found to be identical with the salt obtained from Kerp and Unger's ethyl oxalylaminoacetate (Abstr., 1897, i, 269). The salt, $C_4H_3O_5NCa,4H_2O$, crystallises in white rhombic plates. The statement, however, that this acid is hydrolysed by hydrochloric acid into ammonia and acetic and oxalic acids is controverted, the products obtained being oxalic acid and glycine; the latter was isolated in the form of the hydrochloride of the ester; acetic acid could not be detected. W. R.

Glutamine. ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1906, **65**, 237—246).—Earlier results obtained with glutamine from sugar beet (Schulze and Bosshard, Abstr., 1885, 759) indicated that the substance has no appreciable rotatory power. Sellier (Abstr., 1904, i, 372) has recently examined a preparation which gave $[\alpha]_D^{20}$ +6·15°.

New results with seven preparations of glutamine, from mangolds, pumpkins, mustard, and brake-fern, varied from $[\alpha]_D^{18}$ +1·9 to +9·5°. The variations and the former negative result are attributed to the presence of varying amounts of racemic glutamine.

Solutions of glutamine can be distilled with magnesia at 40° without liberation of ammonia. When boiled with water alone, glutamine yields a considerable amount of ammonia; whilst by boiling in presence of magnesia nearly the whole of the nitrogen of the $CO{\cdot}NH_2$ group is converted into ammonia in two hours. N. H. J. M.

Electrolysis of Aqueous, Acetone, and Pyridine Solutions of Thiocyanates. Part I. STEVENSON BINNING and F. MOLLWO PERKIN (*Trans. Faraday Soc.*, 1906, **2**, 94—97).—On electrolysing a

20% solution of ammonia thiocyanate in water with a current density at the anode of ten amperes per square decimetre, a yellow colouring matter is obtained in 15—20% yield. In the experiments the cathode was rotated within a cylindrical anode, and it was found necessary to remove the colouring matter continuously from the surface of the anode by means of brush-like appendages attached to the cathode. The substance does not appear to be identical with canarine. It blackens when heated with pyridine. When alkaline solutions are electrolysed, the yellow substance is not formed.

Acetone solutions of ammonium thiocyanate also give rise to an orange-yellow substance when electrolysed. This substance dissolves in boiling solutions of alkali hydroxides, and is reprecipitated as a brown, flocculent substance on acidifying with sulphuric acid, hydrogen sulphide being evolved. It is not acted on by strong nitric acid at the ordinary temperature. On boiling with pyridine, a part of it dissolves and the remainder turns black.

Pyridine solutions of the thiocyanate remain clear during electrolysis, but an orange-yellow substance is precipitated when the solution is poured into ten times its volume of water. The substance dissolves in boiling alkali, is reprecipitated by sulphuric acid, and dissolves in nitric acid, from which it is reprecipitated on the addition of water. When a lead anode is used in the pyridine solution, the metal dissolves, and on pouring the solution into water light brown crystals of lead thiocyanate separate. The product is readily soluble in pyridine. H. M. D.

Cyanogen Bromide. THOMAS EWAN (*J. Soc. Chem. Ind.*, 1906, **25**, 1130—1133).—In connexion with the use of cyanogen bromide as a reagent for the extraction of gold from refractory ores, the author has measured the velocity of the reactions $HBrO_3 + 5HBr + 3HCN = 3BrCN + 3HBr + 3H_2O$, $HBrO_3 + 2HBr + 3HCN = 3BrCN + 3H_3O$, $HBrO_3 + 5HBr = 3Br_2 + 3H_2O$. Solutions containing sodium bromate, bromide, and cyanide in quantities corresponding with these equations were heated at 25° and the reaction started by addition of a quantity of hydrochloric acid sufficient to neutralise the cyanide and liberate the bromic and hydrobromic acids. After measured intervals of time, the reaction was stopped by the addition of an excess of sodium hydroxide, which converts the cyanogen bromide into cyanate and bromide; the unchanged cyanide was then titrated with silver nitrate and potassium iodide as indicator, after which the solution was acidified, excess of potassium iodide added, and the iodine liberated by the unchanged bromic acid was titrated.

Assuming that the strong acids are completely dissociated and the hydrocyanic acid undissociated, it is found that the experimental data satisfy the velocity equation $-dC_{BrO_3'}/dt = k[C_{H^{\cdot}}]^2[C_{Br'}][C_{BrO_3'}]$, in which the bracketed symbols denote the concentration of the hydrogen, bromide, and bromate ions respectively. The values obtained for k in the three reactions are practically identical and warrant the conclusion that no secondary change of importance takes place. The interaction between bromic and hydrobromic acids determines therefore the rate of the reaction between bromate, bromide, and cyanide.

When sulphuric acid is used instead of hydrochloric acid, the rate of change is considerably smaller, but this can in all probability be accounted for by the smaller hydrogen dissociation.

Cyanogen bromide has no action on hydrocyanic acid, but reacts quickly with potassium cyanide according to the equation $CNBr + KCN = KBr + C_2N_2$. With alkali hydroxides, carbonates, and water, reaction takes place according to the equation $CNBr + 2OH' = Br' + CNO' + H_2O$. Quantitative measurements of the yield of cyanogen bromide under different conditions show that this approximates to the theoretical value the more closely the experimental conditions approach those indicated by the study of the reaction velocities. H. M. D.

Preparation of Calcium Cyanamide. FREDRIK CARLSON (*Chem. Zeit.*, 1906, **30**, 1261).—The calcium chloride, used in Polzeniusz's method for the preparation of calcium cyanamide (D.R.-P. 1901, 163320), can with advantage be replaced by calcium fluoride; the product is not hygroscopic and can be kept without deterioration for a long time. C. S.

Additive Compounds of Organic Haloids with Silver Nitrate. ROLAND SCHOLL and WILHELM STEINKOPF (*Ber.*, 1906, **39**, 4393—4400).—The compounds of nitriles with metallic salts greatly resemble hydrates. Although a solution of silver nitrate in acetonitrile yields only silver nitrate on evaporation, it has been found possible to isolate additive compounds from halogen derivatives of acetonitrile. The halogen atoms share in the formation of these compounds. A double *compound* of silver nitrate and iodoacetonitrile,

$$AgNO_3,CH_2I\cdot CN,$$

is obtained, together with nitric oxide and silver iodide, when a solution of silver nitrite in acetonitrile is added carefully to a mixture of iodoacetonitrile and acetonitrile at 0°, or in a pure state when the iodoacetonitrile is added drop by drop to a well-stirred aqueous silver nitrate solution. It forms almost colourless crystals, probably orthorhombic, m. p. 121°, and may be recrystallised from water at 50°, but is decomposed into its constituents by boiling water. When distilled it yields *cyanomethyl nitrate*, $CN\cdot CH_2\cdot O\cdot NO_2$, a colourless oil, b. p. 69—70°/13 mm. (slight decomp.), exploding when quickly heated. *Silver nitrate-bromoacetonitrile*, $AgNO_3,CH_2Br\cdot CN$, crystallises in small, almost colourless plates when the aqueous solution is quickly cooled. It sinters and decomposes at 110°. *Silver nitrate-methylene iodide*, $AgNO_3,CH_2I_2$, is a white, crystalline powder, m. p. 80—81°, and only slightly stable. Chloroacetonitrile does not yield an additive compound, and methyl iodide, ethyl iodide, iodoform, and ethyl iodoacetate give Fanto's silver iodide-nitrate (Abstr., 1903, ii, 648).

The paper concludes with a discussion of the nature of these compounds from the standpoint of Werner's theory of supplementary valency (Abstr., 1902, ii, 554) and their importance in the theory of the interaction of organic haloids and silver nitrate (compare Euler, Abstr., 1906, i, 789; Burke and Donnan, Trans., 1904, **85**, 555).

W. R.

New Method of Forming Organic Compounds of Phosphorus. J. Berthaud (*Compt. rend.*, 1906, **143**, 1166—1167).—By the action of white phosphorus (1 atom) on methyl or ethyl alcohol (2 mols.) in a sealed tube at 250° the chief product is the corresponding tetra-alkylphosphonium hydroxide to the extent of 20—30% of the phosphorus employed; the other products are phosphoric acid, the alkyl phosphinic acids, and hydrogen phosphide, together with a small quantity of the alkylphosphines in the case of methyl alcohol, but in the case of ethyl alcohol the quantity of ethylphosphine corresponds with 20% of the original phosphorus.

M. A. W.

Chlorination, in Organic Chemistry, in presence of Thallous Chloride. Victor Thomas (*Compt. rend.*, 1907, **144**, 32—34. Compare Abstr., 1898, i, 640; 1899, i, 26, 676).—Thallous chloride acts similarly to ferric chloride in the chlorination of aromatic hydrocarbons and their haloid derivatives. Benzene gives a mixture of chlorobenzenes. Bromobenzene gives the series of chlorobromobenzenes $C_6H_{[6-(n+1)]}BrCl_n$, but no evidence was obtained of the displacement of bromine by chlorine. From *p*-dibromobenzene the same series of chlorobromobenzenes, $C_6H_{[6-(n+1)]}BrCl_n$, is obtained, one atom of bromine being displaced. In particular, the trichlorobromobenzene, m. p. 138°, is described. Iodobenzene invariably gives a complex mixture of chloroiodobenzenes. Iodine is displaced from only a very small proportion of the iodobenzene, if at all. Among the products isolated are the three isomeric chloroiodobenzenes and a *trichloroiodobenzene*, m. p. 106—107°. The latter gives a mononitro-derivative, m. p. 57·5—58°, probably identical with that described by Istrati (*Bull. Soc. Sci. Bucarest*, **2**, 8), and two polynitro-derivatives. (1) White or very light yellow needles, m. p. 177°, probably a dinitro-compound. (2) Golden-yellow lamellæ resembling lead iodide, very volatile, but melting when thrown on a surface previously heated to 279°, probably a trinitro-compound.

No intermediate additive products could be isolated. Thallous chloride is useless in the chlorination of acetic acid.

E. H.

1-Chloro-2 : 4 : 6-tri-iodobenzene. W. V. Green (*Amer. Chem. J.*, 1906, **36**, 600—604).—1-*Chloro*-2 : 4 : 6-*tri-iodobenzene*, $C_6H_3ClI_3$, prepared from 2 : 4 : 6-tri-iodoaniline by the diazo-reaction, crystallises from a mixture of alcohol and benzene in faintly pink, pyramidal-ended, slender prisms, m. p. 119—120°. When treated with sodium ethoxide it gives up some of its iodine, thus differing in behaviour from the analogous chlorotribromobenzene. Nitric acid converts it into 1-*chloro*-2 : 4 : 6-*tri-iodo*-3 : 5-*dinitrobenzene*, which crystallises from a mixture of benzene and light petroleum in yellowish-white needles, m. p. 266—269°.

T. H. P.

The Sixth Di-iodonitrobenzene. Georg Körner and Angelo Contardi (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 577—579. Compare Abstr., 1906, i, 641).—1 : 2-*Di-iodo*-3-*nitrobenzene*, prepared by a method similar to that used for the synthesis of 1 : 2-dibromo-3-nitrobenzene (*loc. cit.*), crystallises from alcohol in bundles of long needles, m. p. 110·2°, is markedly greener than its isomerides and dissolves in ethyl acetate.

2 : 4-*Di-iodo*-6-*nitroaniline* crystallises from alcohol in slender, orange-yellow needles, m. p. 152°.

6-Iodo-2-nitroaniline crystallises from alcohol in orange-red needles or scales, m. p. 122°. T. H. P.

The Sixth Tribromonitrobenzene and some of its Derivatives. GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 580—588).—3 : 4 : 5-*Tribromoacetanilide*, $C_6H_2Br_3\cdot NHAc$, prepared by the action of bromine on 3 : 5-dibromoacetanilide in acetic acid solution, crystallises from ether in slender, white needles, m. p. 255—256°.

3 : 4 : 5-*Tribromo*-2-*nitroacetanilide*, $NO_2\cdot C_6HBr_3\cdot NHAc$, obtained by the action of sulphuric and nitric acids on 3 : 4 : 5-tribromoacetanilide, crystallises from alcohol or benzene in needles, and from ethyl acetate in mamillary masses of white prisms, m. p. 229—230°.

3 : 4 : 5-*Tribromo*-2-*nitroaniline*, $NO_2\cdot C_6HBr_3\cdot NH_2$, crystallises from alcohol in orange-yellow needles, and from ethyl acetate in tufts of shining, yellowish-red needles, m. p. 134°.

1 : 2 : 3-*Tribromo*-4-*nitrobenzene*, $C_6H_2Br_3\cdot NO_2$, prepared either by the action of ethyl nitrite on 3 : 4 : 5-tribromo-2-nitroaniline in alcoholic solution under pressure or by direct nitration of 1 : 2 : 3-tribromobenzene, crystallises from alcohol in faintly green, satiny needles, m. p. 85·4°, and dissolves readily in benzene, ether, or ethyl acetate.

2 : 3-*Dibromo*-6-*nitroaniline*, $NO_2\cdot C_6H_2Br_2\cdot NH_2$, prepared by the action of alcoholic ammonia on 1 : 2 : 3-tribromo-4-nitrobenzene, crystallises from ethyl acetate in bundles of lanceolated, flattened, dichroic needles which appear red in reflected and yellow in transmitted light, m. p. 149°.

2 : 3 : 4-*Tribromoaniline*, $C_6H_2Br_3\cdot NH_2$, prepared by the reduction of 1 : 2 : 3-tribromo-4-nitrobenzene by means of stannous chloride and hydrochloric acid, is a feeble base crystallising from aqueous alcohol in white lamellæ, m. p. 100·6°.

2 : 3 : 4-*Tribromoacetanilide*, $C_6H_2Br_3\cdot NHAc$, crystallises from alcohol in flattened, white needles, m. p. 160°.

Nitration of 1 : 2 : 3-tribromo-4-nitrobenzene with a mixture of concentrated sulphuric and nitric acids at 130° yields: (1) 1 : 2 : 3-tribromo-4 : 5-dinitrobenzene (compare Jackson and Fiske, Abstr., 1902, i, 362); (2) 1 : 2 : 3-*tribromo*-4 : 6-*dinitrobenzene*, $C_6HBr_3(NO_2)_2$, which crystallises from alcohol in greenish-yellow, flat needles or prisms, m. p. 150°.

2 : 3-*Dibromo*-4 : 6-*dinitroaniline*, $C_6HBr_2(NO_2)_2\cdot NH_2$, obtained on treating 1 : 2 : 3-tribromo-4 : 6-dinitrobenzene with alcoholic ammonia, crystallises in sulphur-yellow needles, m. p. 219°. T. H. P.

A New Method of Reductoin. I. THEODOR WEYL (*Ber.*, 1906, **39**, 4340—4343).—Hydrogen phosphide, obtained from water and red phosphorus, acts as a reducing agent when nascent. Thus, when a mixture of nitrobenzene, red phosphorus, and water is heated at 100° under pressure for several hours, the nitrobenzene is reduced to aniline. In successive experiments the yield of aniline was 24·8, 31·7, 32·5, 64·0, 41·7, 86·2, and 55·5% respectively the duration of heating being 8, 8, 9, 12, 28, 35, and 42 hours. The phosphorus is partly converted into phosphorous and phosphoric acids.

When a mixture of nitrobenzene, red phosphorus, and water is heated at 110—115°, only very little aniline is formed; ammonia, however, is formed in considerable amount.

The reduction of nitrobenzene to aniline is represented by the equation: $3C_6H_5{\cdot}NO_2 + 4PH_3 = 3C_6H_5{\cdot}NH_2 + 2H_3PO_3 + 2P$.

A. McK.

Reduction of Nitrobenzene by Aliphatic Alcohols in Light.

Giacomo L. Ciamician and Paul Silber (*Ber.*, 1906, **39**, 4343—4344).—Aniline and paracetaldehyde do not yield quinaldine in the light, even after one year's exposure; moreover, the formation of quinoline bases in the reduction of nitrobenzene by aliphatic alcohols in light is prevented almost entirely by the absence of acids (compare Abstr., 1906, i, 10).

C. S.

Ammonium and Sodium Sulphides as Partial Reducing Agents for Aromatic Dinitro- and Polynitro-compounds.

Kurt Brand (*J. pr. Chem.*, 1906, [ii], **74**, 449—472).—A systematic investigation of the reduction of aromatic polynitro-compounds by means of sodium sulphide has been undertaken, as accounts of the method occur chiefly in patents and are somewhat scattered in chemical literature. In the present paper, the work of previous authors whose statements are in many cases contradictory is reviewed, and the results of the investigation so far obtained are described.

The reduction of *m*-dinitrobenzene with ammonium hydrogen sulphide, dissolved in a mixture of alcohol and ethyl acetate at 5°, leads to the formation of *m*-nitrophenylhydroxylamine (Abstr., 1906, i, 80), or with sodium sulphide in boiling alcoholic solution to the formation of di-*m*-nitroazoxybenzene and a small amount of *m*-nitroaniline, whilst on reduction with sodium sulphide in alcoholic solution in presence of ethyl acetate the chief product is *m*-nitroaniline, only small amounts of the azoxybenzene being formed (de Bruyn and Blanksma, Abstr., 1901, i, 460; Blanksma, *ibid.*, 461). When boiled with 1 mol. of sodium disulphide in alcoholic solution, *m*-dinitrobenzene is almost completely reduced, the product consisting of *m*-nitroaniline in a yield of 87% and di-*m*-nitroazoxybenzene in a yield of 5·5% of the dinitrobenzene, but with ½ mol. of sodium disulphide 38% of the dinitro-compound is regained unchanged, *m*-nitroaniline being formed to the extent of 35% and di-*m*-nitroazoxybenzene to the extent of 47% of the dinitrobenzene (compare Blanksma, *loc. cit.*; Kunz, Abstr., 1903, i, 813). In boiling alcoholic solution, *m*-dinitrobenzene is reduced almost quantitatively by sodium pentasulphide, forming *m*-nitroaniline, or by sodium hydrogen sulphide forming *m*-nitroaniline and traces of di-*m*-nitroazoxybenzene.

2 : 6-Dinitrotoluene is reduced by sodium hydrogen sulphide in

alcoholic–ethyl acetate solution, forming 6-nitro-2-aminotoluene, together with traces of 2 : 6-tolylenediamine; 2 : 4-dinitrotoluene is reduced similarly to 2-nitro-4-aminotoluene, together with smaller quantities of 4-nitro-2-aminotoluene, the total yield of nitroamines amounting to 80% of the theoretical.

The action of sodium hydrogen sulphide on 2 : 4-dinitroaniline leads to the formation of 4-nitro-*o*-phenylenediamine and traces of nitro-*p*-phenylenediamine, or on picric acid to the formation of picramic acid. G. Y.

The Two Modifications of *o*-Nitrotoluene. Iwan von Ostromisslensky (*Zeit. physikal. Chem.*, 1906, **57**, 341—348).—When freshly-distilled *o*-nitrotoluene is rapidly cooled to −20°, it solidifies sometimes to the labile α-modification (m. p. −10·56°), sometimes to the stable β-modification (m. p. −4·14°). Superheating of the vapour during distillation favours the subsequent separation of the β-modification. Another method for preparing the latter is to cool the liquid substance to −50° or −60°; the primary crystallisation from the cooled liquid consists of the α-modification, but after a short time this changes spontaneously into the β-modification. At all temperatures not too close to the melting point of the α-modification, the change $\alpha \longrightarrow \beta$ takes place, so that the two modifications are monotropic. It is probable, however, that the transition point is close to the melting point of the α-form.

The freezing point depression constants are found to be: for the α-form, 50·8; for the β-form, 71·8. The molecular weights of iodine and sulphur dissolved in the β-form are found by the freezing point method to correspond with I_5 and $S_{10}-S_{11}$ respectively.

Allied substances existing in two modifications (the m. p's. of which are Δ° apart) are *o*-chlorotoluene ($\Delta = 5·8°$), *o*-toluidine ($\Delta = 5°$), *o*-chlorophenol ($\Delta = 7°$), *o*-bromotoluene ($\Delta = 5·1°$). The two modifications of *o*-chlorotoluene are enantiotropic; at −50° the change $\alpha \longrightarrow \beta$ takes place, at −17° the change $\beta \longrightarrow \alpha$; the transition temperature lies therefore between −17° and −50°. J. C. P.

Nitration of Aniline and of certain of its Derivatives. J. Bishop Tingle and F. C. Blanck (*Amer. Chem. J.*, 1906, **36**, 605—610).—Attempts were made to nitrate aniline (or aniline nitrate) directly by the action of 99% nitric acid free from nitrous acid, but although carbamide was added to decompose any nitrous acid formed and the reactions were carried out in platinum vessels immersed in a freezing mixture, it was found to be impossible to keep the temperature sufficiently low, tarry or carbonaceous products being always formed.

Nitric acids of 50·71—75·33% concentrations give with aniline a pink solid, stable at 0°, the colour being instantly discharged by the addition of a little water or aniline. Slight excess of acid increased or restored the colour, and, if the added acid were sufficiently concentrated, the pink colour darkened until it became black, the whole mass gradually charring and sometimes incandescing. With nitric acids of concentrations up to 75·33%, any charring produced is due to attack of the aniline nitrate and not of the nitrate. The readiness of nitration of aniline by means of nitric and sulphuric acid hence cannot be due to "protection" of the amino-group by the sulphuric acid, as this group is equally well "protected" in aniline nitrate.

Experiments were also made on the action on anilines substituted in the amino-group of 80% nitric acid (D 1·46) in presence of acetic, oxalic, trichloroacetic, or 92% sulphuric acid (D 1·83). The results show that the position assumed by the entrant nitro-group is definitely influenced both by the acid present with the nitric acid and by the amino-substituent. T. H. P.

Preparation of Simple Aromatic Cyanamides. PAUL PIERRON (*Bull. Soc. chim.*, 1906, [iii], **35**, 1197—1204).—The method of preparation described by Cloez and Cannizzaro (*Compt. rend.*, 1851, **32**, 62) gives good results in the case of naphthalene derivatives, whilst a modification of that proposed by Hofmann (*Ber.*, 1869, **2**, 600, and 1870, **3**, 264) furnishes better results in the case of benzene derivatives, especially when the desulphuration of the thiocarbamides is accomplished by the use of cupric sulphate in place of litharge.

m-*Tolylcyanamide*, prepared from *m*-tolylthiocarbamide by the modification of Hofmann's method referred to, is a viscous, nearly colourless liquid, which in contact with water forms a hydrate (m. p. 27°) (compare Heller and Bauer, Abstr., 1902, i, 444), and in contact with hydrochloric acid furnishes *m*-tolylcarbamide (m. p. 142°).

α-Naphthylcyanamide and the isomeric β-compound were prepared by Cloez and Cannizzaro's method, cyanogen bromide being employed instead of cyanogen chloride. m-*Ethoxyphenylcyanamide* was also prepared by this method, alcohol being employed as a solvent for the *m*-ethoxyaniline in place of ether. It crystallises in colourless needles, m. p. 57°, and is readily hydrolysed by acids to the corresponding *carbamide*, which crystallises in colourless, flattened needles, m. p. 112°. *m*-Ethoxyphenylcarbamide is also readily obtained by the action of potassium cyanate on *m*-aminophenetole hydrochloride.

o-*Bromophenylcyanamide*, similarly obtained, crystallises in brilliant, slender, colourless needles, m. p. 94°, and by boiling its solution in alcohol with hydrochloric acid is transformed into the corresponding *carbamide*, which crystallises in colourless, flattened needles, m. p. 202°, and by repeated evaporation with hydrochloric acid furnishes ammonia, *o*-bromoaniline, and carbon dioxide. m-*Bromophenylcyanamide*, similarly obtained from *m*-bromoaniline, crystallises from benzene in brilliant, colourless lamellæ, m. p. 84°, is readily soluble in alcohol and less so in ether, and with acids yields *m*-bromophenylcarbamide (compare Folin, Abstr., 1897, i, 470). p-*Bromophenylcyanamide*, prepared from *p*-bromoaniline, crystallises in colourless, long, slender, prismatic needles, m. p. 112°, is very soluble in alcohol, fairly so in ether, less so in chloroform, and slightly so in water; it is readily soluble in alkalis and insoluble in dilute acids.

Hofmann's method is not applicable to the preparation of the bromophenylcyanamides, owing to the difficulty of preparing the necessary thiocarbamides. T. A. H.

Influence of Certain Substituting Groups on the Oxidation of Tertiary Amines to Amine Oxides. EUGEN BAMBERGER and LEO RUDOLF (*Ber.*, 1906, **39**, 4285–4293. Compare Abstr., 1902, i, 364; Bamberger and Tschirner, Abstr., 1899, i, 347).—The amount of amine oxides, formed by the oxidation of tertiary aromatic bases by means of Caro's acid, varies with the alkyl groups attached to the nitrogen atom and with the absence or presence and position of methyl groups in the benzene nucleus. In comparative experiments, 10 grams each of dimethylaniline, dimethyl-*p*-toluidine, dimethyl-*o*-toluidine, diethylaniline, *vm*-dimethylxylidine, and dimethylmesidine yielded 11·1, 10·9, 7·16, 6·89, 0, and 0 grams respectively of the corresponding amine oxides; in a second series of experiments in more dilute solution, of 10 grams each of dimethylaniline, dimethyl-*o*-toluidine, dimethyl-*p*-toluidine, diethylaniline, diethyl-*o*-toluidine, and diethyl-*p*-toluidine, 0·0, 6·35, 0·3, 6·43, 8·84, and 6·18 respectively, remained unoxidised; whilst in a third series of 10 grams each of diethyl-*o*-toluidine and diethyl-*p*-toluidine, 8·7 and 5·8 grams respectively, remained unchanged. The oxidation takes place more easily with dimethyl- than with diethyl-aniline, is hindered by the presence of an *o*-methyl group, and is prevented by the presence of two *o*-methyl groups.

The action of methyl sulphate on mesidine leads to the formation of dimethyl- and methyl-mesidines, which are separated by conversion of the latter into its *acetyl* derivative, $C_6H_2Me_3{\cdot}NMeAc$; this crystallises in glistening prisms, m. p. 51—51·5°, b. p. 150—150·5°/13 mm. Dimethylmesidine is colourless, b. p. 213·3—213·5°/716 mm., $D_4^{20\cdot5}$ 0·905 (Hofmann, *Ber.*, 1872, **5**, 718 : b. p. 213—214°, D 0·9076), but after treatment with Caro's acid is slightly yellow, $D_4^{21\cdot2}$ 0·9076.

vm-Dimethylxylidine, prepared together with *vm*-methylxylidine by the action of methyl sulphate on *vm*-xylidine, is colourless, b. p. 192·5—192·8°/716 mm. or 76·8—77·2°/11 mm., $D_4^{20\cdot5}$ 0·912 (b. p. 196°, D 0·9296 : Hofmann, *loc. cit.*, 712; b. p. 195—196° : Friedländer, Abstr., 1899, i, 350), but after treatment with Caro's acid is yellow, $D_4^{21\cdot2}$ 0·914. Contrary to Friedländer's statement (*loc. loc.*), the base does not react with nitrous acid. G. Y.

Asymmetric Nitrogen. XXVI. Optically Active Phenylbenzylmethylethyl Ammonium Bases. EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1906, **39**, 4437—4442. Compare Abstr., 1906, i, 161, 162).—The values $[M]_D$ +17·3 for the active cation $NMeEtPh{\cdot}C_7H_7$, obtained by Wedekind (*Ber.*, 1907, **37**, 2727), and $[M]_D$ +19·3, obtained by H. O. Jones (Trans., 1904, **85**, 225), appear too low in view of the values $[M]_D$ +285 for the active cation $NMePrPh{\cdot}C_7H_7$ and $[M]_D$ −279 for the corresponding *iso*butyl base (compare Abstr., 1905, 878).

Phenylbenzylmethylethylammonium bromide forms prisms, m. p. 158—159°; it was not found possible to resolve it by crystallisation of the *d*-bromocamphorsulphonate. By continued fractional crystallisation of a large quantity of the *d*-camphorsulphonate, a fraction $[M]_D$ +116·1° was obtained equivalent to $[M]_D$ +64·4° for the cation $NMeEtPh{\cdot}C_7H_7$.

The ammonium iodide prepared from this fraction had $[\alpha]_D$ +41·4° in alcohol, and did not alter when kept; in chloroform, $[\alpha]_D$ +56·5°, autoracemisation quickly set in. E. F. A.

Preparation of s-Hexanitrodi-m-xylylamine. JAN J. BLANKSMA (*Rec. trav. chim.*, 1906, **25**, 373—375).—5-*Bromo*-2 : 4 : 6-*trinitro*-m-*xylene*, which forms colourless crystals, m. p. 224°, is obtained by nitrating 5-bromo-*m*-xylene; when heated with *m*-xylidine in alcoholic solution it yields 2 : 4 : 6-trinitro-di-1 : 3 : 5-xylylamine, which on nitration is converted into s-*hexanitrodi*-1 : 3 : 5-*xylylamine*, m. p. 222°. This substance separates from chloroform in glistening crystals which contain 1 molecule of the solvent. P. H.

Hydroxamic Acids. RAYMOND MARQUIS (*Compt. rend.*, 1906, **143**, 1163—1165. Compare Abstr., 1905, i, 524).—Thiele and Pickard (Abstr., 1900, i, 29) explain the formation of symmetrical disubstituted carbamides from the alkali salts of the dihydroxamic acids (Lossen, Abstr., 1894, i, 415) on the assumption that the acid undergoes the Beckmann rearrangement, with the formation of a carbimide, which is converted into the carbamide by the action of water. The author has examined the behaviour of hydroxamic acid towards reagents which induce the Beckmann rearrangement and finds that in certain cases the reaction is normal. Thus, benzhydroxamic acid yields phenylcarbamide when treated with thionyl chloride in the presence of boiling benzene, and salicylhydroxamic acid when similarly treated yields oxycarbanil (Ransom, Abstr., 1898, i, 415), the acetyl derivative of which has m. p. 91° [Kalckhoff gives 95° (Abstr., 1883, 734) and Bender gives 97·98° (Abstr., 1887, 37)].

Phenyl-*p*-tolylcarbamide, obtained by the condensation of phenylcarbamide and *p*-toluidine, m. p. 218°, then solidifies and melts sharply at 221° [Paal and Valvolxem (Abstr., 1894, i, 621) give 212° and Dixon (Trans., 1901, **79**, 103) gives 215°].

Phenylcarbamylbenzhydroxamic acid, $\mathrm{OH\cdot CPh{:}NO\cdot CO\cdot NHPh}$, obtained by the condensation of phenylcarbamide and benzhydroxamic acid in pyridine solution, crystallises from alcohol in small needles, m. p. 209—210°; *phenylcarbamylsalicylhydroxamic acid*,

$$\mathrm{OH\cdot C_6H_4\cdot C(OH){:}NO\cdot CO\cdot NHPh},$$

crystallises from benzene and alcohol in flat, pearly needles, m. p. 181°, which rapidly redden in the light. M. A. W.

Preparation of Aromatic Thiocarbamides by the Hydrogen Peroxide Method. JULIUS VON BRAUN and ERICH BESCHKE (*Ber.*, 1906, **39**, 4369—4378. Compare Abstr., 1900, i, 644; 1902, i, 271).—Continuing the work on the mechanism of the reaction between primary aromatic amines and carbon disulphide in the presence of hydrogen peroxide, the authors have applied the method in the following cases.

m- and *p*-Toluidine, *p*-cumidine, 1 : 3 : 4-xylidine, and *p*-aminobenzyl cyanide react within a few minutes. *Dicumylthiocarbamide* has m. p. 149°; *ω-dicyanoditolylthiocarbamide*, m. p. 191°, is insoluble in alcohol.

o- and *p*-Chloroanilines react after two days, whereas the meta-isomeride undergoes a rapid conversion into the carbamide. *m*-Bromoaniline readily yields the *carbamide*, m. p. 128°, whilst *p*-bromoaniline and *p*-iodoaniline require many hours.

p-Anisidine and *p*-phenetidine react as readily as aniline itself, *o*-anisidine only very slowly.

Methyl anthranilate and ethyl *p*-aminobenzoate yield the corresponding *carbamides* after many days, but they have not yet been examined completely. C. S.

Decomposition of Dinitrophenyl Thiocyanate. Oscar Hinsberg (*Ber.*, 1906, **39**, 4331—4332).—According to Austen and Smith (Abstr., 1886, 693), dinitrophenyl thiocyanate, obtained by the action of potassium thiocyanate on 4-bromo-1 : 3-dinitrobenzene, forms dinitrophenyl mercaptan, m. p. 195°, when warmed with concentrated sulphuric acid. According to the author, this observation is not correct, since the product of the action in question is not uniform, but a mixture of 2 : 4-dinitrophenyl mercaptan, m. p. 131°, and 2′ : 4′-tetranitrodiphenyl disulphide.

The observation of Austen and Smith that, when dinitrophenyl thiocyanate is warmed with a mixture of concentrated sulphuric acid and fuming nitric acid, a tetranitrodiphenyl sulphide, m. p. 245°, is produced is also erroneous. A. McK.

Use of Compounds of Bases with Sulphurous Acid as Photographic Developers. Auguste Lumière, Louis Lumière, and Alphonse Seyewetz (*Bull. Soc. chim.*, 1906, [iii], **35**, 1204—1207).—Compounds of this type with *p*-aminophenol, *p*-methylaminophenol, and *p*-phenylenediamine have been obtained (1) by the action of sulphur dioxide on the free bases suspended in warm water, (2) by cooling warm solutions of the bases in "liquid commercial sodium bisulphite" (40%), or (3) by heating *p*-methylaminophenol sulphate with a solution of anhydrous sodium sulphite to which one-fourth of its volume of sodium hydrogen sulphite had been added.

The *product*, $10OH\cdot C_6H_4\cdot NH_2,H_2SO_3$, obtained with *p*-aminophenol occurs in white crystals having a faint odour of sulphur dioxide and does not become brown on exposure to air.

The *compound*, $6OH\cdot C_6H_4\cdot NHMe,H_2SO_3$, yielded by *p*-methylaminophenol, occurs in small white crystals, is stable in air, has no odour of sulphur dioxide, and has m. p. 87°, evolving sulphur dioxide.

The *compound*, $9C_6H_4(NH_2)_2,H_2SO_3$, obtained from *p*-phenylenediamine, forms small white crystals having a feeble odour of sulphur dioxide, is stable in air, and has m. p. 137°, evolving sulphur dioxide.

These three substances are comparable as developers with the three bases from which they are derived, and the solubility in water of the *p*-methylaminophenol product enables it to be used as a developer by the addition of sodium sulphite. T. A. H.

Action of Bromine and Chlorine on Phenols. Substitution Products, ψ-Bromides, and ψ-Chlorides. XX. Action of Bromine on *o*-Cresol. Theodor Zincke and August von Hedenström (*Annalen*, 1905, **350**, 269—287. Compare Abstr., 1906, i, 739).—*o*-Cresol reacts readily with the calculated quantities of bromine alone or in presence of iron in chloroform or carbon tetrachloride solution, forming mono-, di-, tri-, and tetra-bromo-derivatives.

The *acetyl* derivative of 5-bromo-*o*-cresol (Claus and Jackson, Abstr., 1889, 128) is an oil. The *acetyl* derivative of 3 : 5-dibromo-*o*-cresol (*loc. cit.*) crystallises in glistening needles, m. p. 62°.

3 : 4 : 5-(or 3 : 5 : 6-)*Tribromo-o-cresol*, $C_6HMeBr_3\cdot OH$, crystallises from light petroleum in long, colourless needles, m. p. 79°; the *acetyl* derivative crystallises in glistening needles, m. p. 72—73°.

Tetrabromo-o-cresol, $C_6MeBr_4\cdot OH$, crystallises in glistening needles, m. p. 205°; the *acetyl* derivative forms glistening needles, m. p. 154°.

The action of sodium nitrite on these bromo-*o*-cresols in glacial acetic acid solution leads to the formation of bromonitro-derivatives. 5-Bromo- and 3 : 5-dibromo-*o*-cresols yield 5-bromo-3-nitro-*o*-cresol (Wroblewski, this Journal, 1874, 27, 52).

4 : 5-*Dibromo-3-nitro-o-cresol*, $C_7H_5O_3NBr_2$, formed from 3 : 4 : 5-tribromo-*o*-cresol, crystallises in yellow needles, m. p. 141° (decomp.).

4 : 5 : 6-*Tribromo-3-nitro-o-cresol*, $NO_2\cdot C_6MeBr_3\cdot OH$, formed from tetrabromo-*o*-cresol, crystallises in yellow, monoclinic prisms, m. p. 156° (decomp.).

The action of bromine on 5-bromo- or 3 : 5-dibromo-*o*-cresol at 170° leads to the formation of 3 : 5-dibromo-*o*-cresol ψ-bromide,

$$OH\cdot C_6H_2Br_2\cdot CH_2Br$$

or $C_6H_3OBr_2\cdot CH_2Br$ (Auwers and Büttner Abstr., 1899, i, 36).

3 : 4 : 5-*Tribromo-o-cresol ψ-bromide*, $C_7H_4OBr_4$, formed by heating the tribromo-cresol with bromine in a sealed tube in the water bath, crystallises in monoclinic needles or prisms, m. p. 134°, reacts only very slowly with alkali hydroxides, and when shaken in ethereal solution with dilute alkali hydroxides forms a white, amorphous, polymeric *methylenequinone*. Reduction of the ψ-bromide with zinc and hydrogen bromide in glacial acetic acid solution leads to the formation of 3 : 4 : 5-tribromo-*o*-cresol. The *acetyl* derivative, $OAc\cdot C_6HBr_3\cdot CH_2Br$, forms glistening needles, m. p. 137°.

3 : 4 : 5-*Tribromo-2-hydroxybenzyl alcohol*, $OH\cdot C_6HBr_3\cdot CH_2\cdot OH$, prepared by boiling the ψ-bromide with aqueous acetone, crystallises in stellate aggregates of needles, m. p. 141°; the *diacetyl* derivative,

$$C_{11}H_9O_4Br_3,$$

crystallises in glistening needles, m. p. 92°. The *methyl ether*,

$$OH\cdot C_6HBr_3\cdot CH_2\cdot OMe,$$

prepared by boiling the ψ-bromide with methyl alcohol, crystallises in glistening needles, m. p. 81—82°; the *acetyl* derivative forms white needles, m. p. 90—91°. When boiled for a few minutes with acetic acid and sodium acetate, the ψ-bromide forms the *acetyl* derivative,

$$C_6H_2OBr_3\cdot CH_2\cdot OAc,$$

which crystallises in glistening needles, m. p. 130—131°, on hydrolysis yields tribromohydroxybenzyl alcohol, and forms the diacetyl derivative of this when heated with sodium acetate and acetic anhydride.

Tetrabromo-o-cresol ψ-bromide, $C_6HOBr_4\cdot CH_2Br$, or $OH\cdot C_6Br_4\cdot CH_2Br$, formed by heating the tetrabromocresol with bromine in a sealed tube at 100°, crystallises in colourless needles, m. p. 156°, yields a white, amorphous *product* when shaken with ether and a dilute alkali hydroxide, and if shaken with benzene and a dilute alkali hydroxide forms the amorphous substance and a yellow solution which on evaporation deposits a yellow *residue*, probably the *o*-methylenequinone. The *acetyl* derivative, $OAc\cdot C_6Br_4\cdot CH_2Br$, formed by boiling the ψ-bromide with acetic anhydride, crystallises in small, hard needles, m. p. 156°. *Tetrabromo-*o*-hydroxybenzyl alcohol*, $C_7H_7O_2Br_4$, crystallises in small needles, m. p. 158° (decomp.); the *diacetyl* derivative, $C_{11}H_8O_4Br_4$, crystallises in glistening needles, m. p. 138—139°. The *methyl ether*, $C_8H_6O_2Br_4$, forms white needles, m. p. 94—95°; the *acetyl* derivative forms glistening needles, m. p. 98—99°.

The *acetyl* derivative, $C_6HOBr_4\cdot CH_2\cdot OAc$, prepared by boiling the ψ-bromide with glacial acetic acid and sodium acetate, forms white needles, m. p. 133°, on hydrolysis yields tetrabromo-*o*-hydroxybenzyl alcohol, and the diacetate of this when boiled with acetic anhydride and sodium acetate. G. Y.

m-Tolyl Ether and Derivatives. ALFRED N. COOK (*Amer. Chem. J.*, 1906, **36**, 543—551. Compare Gladstone and Tribe, Trans., 1882, **41**, 11).—*Aluminium* m-*tolyloxide*, prepared by the action of commercial aluminium on *m*-cresol, is a brittle, grey to black, translucent solid, having a vitreous lustre and a conchoidal fracture. When distilled in a vacuum, it yields a small quantity of *m*-cresol and a large proportion of a substance, b. p. 240°/30 mm., but under ordinary pressure it gives *m*-cresol, *m*-tolyl ether, a solid, b. p. about 300° (uncorr.), and a red liquid, b. p. about 360°.

m-Tolyl ether has b. p. 290·5—291·5° and D^{21} 1·0323 and its viscosity is 1·333 at 15·5°, 1·194 at 30°, 1·166 at 40°, and 1·139 at 50°; its viscosity is hence 9·4% greater than that of phenyl ether (1·095) at 30°, in spite of its lower specific gravity. It is volatile in a current of steam. Chromic acid in glacial acetic acid oxidises it to a white powder insoluble in alkalis. *Dibromo-*m*-tolyl ether*, $O(C_6H_3BrMe)_2$, is a white, crystalline substance, m. p. 48°, b. p. 250°/15 mm. and 340—350° (uncorr.) at ordinary pressure. *Tetrabromo-*m*-tolyl ether*,

$$O(C_6H_2Br_2Me)_2,$$

is a pale yellow, sticky, viscous substance crystallising in nodular aggregates, b. p. 260—270°/35 mm. *Dinitro-*m*-tolyl ether*,

$$O(C_6H_3Me\cdot NO_2)_2,$$

separates from alcohol in yellow crystals, m. p. 112—113°. *Diamino-*m*-tolyl ether hydrochloride*, $O(C_6H_3Me\cdot NH_2,HCl)_2$, was prepared and also the free *base*. T. H. P.

Nitration of Meta-Substituted Phenols. JAN J. BLANKSMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 278—280).—The nuclear hydrogen atoms in *m*-nitrophenols, containing a hydroxyl, methyl, methoxy-, or ethoxy-group, or chlorine or bromine in position 5, are readily substituted by three atoms of bromine by treatment with bromine water, or by three nitro-groups by nitration by nitric acid (D 1·52) and sulphuric acid. The tetranitro-compounds separate from a mixture of these acids in colourless crystals, turn yellow in the presence of water, have a bitter taste, and an acid reaction, and are explosive. If the phenolic hydrogen atom is replaced by methyl, only two nitro-groups can be introduced.

By boiling water, *tetranitro*-m-*cresol*, m. p. 175°, is converted into trinitro-orcinol, whilst *tetranitroresorcinol*, m. p. 152°, *chlorotetranitrophenol*, m. p. 147°, or *bromotetranitrophenol*, m. p. 157°, yield trinitrophloroglucinol.

5-*Nitroresorcinol* has m. p. 158°, and the *ethyl ether*, m. p. 80°; the *tetranitro-methyl* and *ethyl ethers* have respectively m. p. 115° and 110°; 3-*chloro*-5-*nitrophenol*, m. p. 147°, and the *bromo*-compound, m. p. 145°. C. S.

Synthesis of αδ-Halogen Ethers and of αδ-Dihalogen Derivatives of Butane. Julius von Braun and Erich Beschke (*Ber.*, 1906, **39**, 4357—4362).—αδ-Dichloro- or -dibromo-butane can be obtained in 10% yield by reducing succinonitrile with sodium and alcohol, benzoylating the product, and treating the resulting mixture with phosphorus pentachloride or pentabromide.

Benzo-δ-phenoxybutylamide (compare this vol., i, 80) and phosphorus pentachloride in molecular quantities react to form ultimately *α-chloro-δ-phenoxybutane*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CH_2\cdot OPh$, which is a colourless, refractive, pleasant-smelling liquid, b. p. 147°/12 mm., and reacts with sodium phenoxide to form Grignard's αδ-diphenoxybutane (Abstr., 1904, i, 494).

αδ-Dichlorobutane, $C_4H_8Cl_2$, b. p. 53—58°/12 mm., is obtained from the preceding chlorinated ether and concentrated hydrochloric acid above 130°.

α-Iodo-δ-phenoxybutane, $CH_2I\cdot[CH_2]_2\cdot CH_2\cdot OPh$, obtained from the chlorinated ether and sodium iodide in alcoholic solution, forms white leaflets, m. p. 43—44°, b. p. 155—160°/15 mm., and is changed quantitatively by hydriodic acid at 100° into αδ-di-iodobutane.

αδ-Dibromobutane cannot be obtained from phosphorus pentabromide and benzo-δ-phenoxybutylamide, but is prepared readily from αδ-diphenoxybutane and hydrobromic acid at 130—140°. C. S.

Constitution and Colour of Nitrophenols. Hugo Kauffmann (*Ber.*, 1906, **39**, 4237—4242. Compare Abstr., 1900, i, 480; 1901, i, 318; 1906, i, 577; Kauffmann and Franck, Abstr., 1906, i, 841).—A reply to Hantzsch (Abstr., 1906, i, 353, 833; Ley and Hantzsch, *ibid.*, 790). Nitroquinol dimethyl ether is a very stable substance, and its yellow colour cannot be attributed to the presence of nitroquinol. Its solution in light petroleum is colourless, but deposits yellow crystals. Free nitroquinol dissolves in light petroleum to a yellow solution. G. Y.

Nitroquinol Dimethyl Ether. Hugo Kauffmann and Imanuel Fritz (*Ber.*, 1906, **39**, 4243—4248. Compare Kauffmann, Abstr., 1906, i, 577; preceding abstract; Hantzsch, Abstr., 1906, i, 353, 833).—When prepared by nitration of quinol dimethyl ether, nitroquinol dimethyl ether contains traces of a hydrolytic product, probably the monomethyl ether, which is removed completely on recrystallisation from alcohol. The pure dimethyl ether is yellow, and is unchanged on addition of an alkali hydroxide, whereas 0·007 gram of the hydrolytic product dissolved in 1 litre of water gives a distinct change of colour. The solubility of the dimethyl ether in water is diminished by the addition of sodium carbonate. It yields only traces of hydrolytic products when treated at the laboratory temperature with concentrated, or boiled with dilute, sulphuric acid; a *substance* crystallising in orange-red needles, m. p. 79—80°, is formed on boiling with aqueous or alcoholic alkali hydroxides. The dimethyl ether is hydrolysed only slowly by aluminium chloride in boiling light petroleum or benzene solution, and is decomposed in boiling toluene solution. G. Y.

Methylene and Other Derivatives of *m*-Dihydroxybenzenes. A. Luther (*Arch. Pharm.*, 1906, **244**, 561—568).—Methylenediresorcinol, $CH_2[C_6H_3(OH)_2]_2$, is broken down by prolonged boiling with zinc dust and aqueous sodium hydroxide; the formation (in about 20% yield) of cresorcinol, $C_6H_3Me(OH)_2$ [$Me:(OH)_2=1:2:4$], and resorcinol was ascertained by first treating the product with sodium nitrite and nitrous oxide, then oxidising with nitric acid of D 1·3, and, finally, crystallising from water, when dinitroresorcinol, m. p. 142°, and dinitrocresorcinol, m. p. 90°, crystallised in succession. Cresorcinol forms a *mono-* and a *di-benzoyl* derivative, m. p. 115—116° and 83°, and a *diacetyl* derivative, b. p. 293—295°; with bromine in chloroform solutions it yields *dibromocresorcinol*, $C_7H_6O_2Br_2$, m. p. 86—87°, with bromine and water, *tetrabromocresorcinol*, $C_7H_4O_2Br_2$, m. p. 99—100°, and in chloroform solution with gaseous chlorine, *tetrachlorocresorcinol*, $C_7H_4O_2Cl_4$, m. p. 69—70°, which yields *dichlorocresorcinol*, $C_7H_6O_2Cl_2$, m. p. 78—79°, when reduced with stannous chloride and hydrochloric acid; with diazoaminobenzene in alcoholic solution it condenses to the scarlet cresorcinolbisazobenzene,

$$C_{19}H_{16}O_2N_4,$$

m. p. 211—212°; and with formaldehyde it yields methylenedicresorcinol, m. p. 195—200°.

The last substance, $CH_2[C_6H_2Me(OH)_2]_2$, is broken down by reduction with zinc dust and aqueous sodium hydroxide to xylorcinol, $C_6H_2Me_2(OH)_2[Me_2:(OH)_2=1:3:4:6]$, and cresorcinol, which can be separated by fractional crystallisation from hot benzene. Xylorcinol, which can crystallise with $1H_2O$, forms a *dibenzoyl* derivative, m. p. 155°; with bromine in chloroform solution it yields *bromoxylorcinol*, $C_8H_9O_2Br$, m. p. 119—120°; with diazoaminobenzene it does not condense; with formaldehyde and dilute sulphuric acid it yields *methylenedixylorcinol*, $C_{17}H_{20}O_4$, m. p. 251°, which crystallises with $1H_2O$.

The last substance is not attacked by zinc dust and aqueous sodium hydroxide. The same is true of *methylenedis*-4:6-*dihydroxy*-1:2:3-*trimethylbenzene*, $C_{19}H_{24}O_4$, m. p. 228°, which was obtained from 4:6-dihydroxy-1:2:3-trimethylbenzene (Simon, Abstr., 1904, i, 406) and formaldehyde in the presence of dilute sulphuric acid.

C. F. B.

Action of Organo-Magnesium Haloids on Acetylenic Aldehydes and Ketones. Acetylenic Alcohols. Maurice Brachin (*Bull. Soc. chim.*, 1906, [iii], **35**, 1163—1179).—Phenylpropiolaldehyde, obtained by condensing the sodium derivative of phenylacetylene with ethyl formate (compare Moureu and Delange, Abstr., 1901, i, 581), reacts with magnesium methyl iodide in presence of ether, forming the *additive* compound CPh⋮C·CHMe·OMgI,Et$_2$O, a yellowish-white, deliquescent powder, which when suspended in ether and the mixture poured into water containing acetic acid, decomposes, forming phenylacetylenemethylcarbinol, CPh⋮C·CHMe·OH (compare Moureu and Desmots, Abstr., 1902, i, 289), which has b. p. 132—134°/16 mm., D_0^0 1·0449, $D_4^{12\cdot6}$ 1·0363, $n_D^{12\cdot6}$ 1·57305, and reacts with mercuric chloride in alcohol, yielding the *product* CPh⋮C·CHMe·OHgCl, which crystallises in faintly yellow, prismatic needles, has m. p. 111°, and on hydrolysis with dilute sulphuric acid regenerates the parent alcohol.

Phenylpropioaldehyde reacts with magnesium ethyl bromide, forming *a-phenyl-Δ^a-pentinene-γ-ol*, CPh⋮C·CHEt·OH, a faintly yellow oil having b. p. 141—143°/15 mm., D_0^0 1·0298, D_4^{13} 1·0138, and n_D^{13} 1·5633. With magnesium propyl iodide, phenylpropiolaldehyde yields *a-phenyl-Δ^a-hexinene-γ-ol*, CPh⋮C·CHPr^a·OH, an amber-coloured oil, which has b. p. 149—152°/17 mm., D_0^0 1·0180, and decomposes when kept. *a-Phenyl-ε-methyl-Δ^a-hexinene-γ-ol*, CPh⋮C·CH(OH)·CH$_2$·CHMe$_2$, similarly obtained by means of magnesium *iso*butyl iodide, is a slightly coloured oil, has b. p. 149—151°/16 mm. and D^0 1·0148. With phenyl magnesium bromide, aγ-diphenylpropinyl alcohol, CPh⋮C·CHPh·OH, is obtained; it is a colourless oil, has b. p. 208·5—209·5°(corr.)/15 mm., D_0^0 1·1127, $D_4^{17\cdot05}$ 1·0964, and $n_D^{17\cdot5}$ 1·6173 (compare Moureu and Desmots, *loc. cit.*). The *additive* product, CPh⋮C·CHPh·OMgBr,Et$_2$O, initially formed in the foregoing reaction, is crystalline.

No acetylenic alcohols are formed when amylpropiolaldehyde reacts with organo-magnesium haloids.

Propionylphenylacetylene, CPh⋮C·COEt (compare Moureu and Brachin, Abstr., 1904, i, 95), reacts with magnesium methyl iodide in presence of ether, forming a crystalline *product*, which on decomposition by water yields the tert.-*alcohol*, CPh⋮C·CMeEt·OH, and this on distillation furnishes *phenylbutenylacetylene*, CPh⋮C·CEt:CH$_2$ or CPh⋮C·CMe:CHMe. This is a colourless liquid with a geraniol-like odour, has b. p. 113—115°/15 mm., D^0 0·9452, D_4^{13} 0·93, and n_D^{13} 1·5828.

Butyrylphenylacetylene, CPh⋮C·COPr (*loc. cit.*), reacts with magnesium ethyl bromide, forming *phenylacetylene-ethylpropylcarbinol*, CPh⋮C·CEtPr·OH, which has b. p. 155—157°/16 mm. and D^0 0·9885.

T. A. H.

Stigmasterol, a new Phytosterol from the Calabar Bean. ADOLF WINDAUS and A. HAUTH (*Ber.*, 1906, **39**, 4378—4384).—Phytosterol (m. p. 130), prepared according to Hesse's directions (Abstr., 1878, 850), is shown not to be a single substance, as successive extractions by solvents result in the m. p. of the residue being gradually raised. The bromine additive product obtained from the acetate is easily resolved into two different bromides by fractional crystallisation from glacial acetic acid, alcohol, acetone, or ether. By careful treatment with zinc dust and acetic acid, the unsaturated acetates are recovered and the alcohols obtained by hydrolysis with alcoholic potash. They have a constant m. p. and behave as chemical entities; 80% of the mixture consists of phytosterol, identical with the phytosterol obtained from germinating wheat and with sitosterol (Burián, Abstr., 1898, i, 72; Ritter, Abstr., 1902, i, 446). The remainder consists of an alcohol, *stigmasterol*, $C_{30}H_{48}O,H_2O$ or $C_{30}H_{50}O,H_2O$, with m. p. 170°, $[\alpha]_D^{21}$ $-45{\cdot}01°$ in chloroform, and $[\alpha]_D^{24}$ $-44{\cdot}67°$ in ethyl ether; it is isomorphous with phytosterol, forms mixed crystals with it, and gives the same colour reactions. The crude phytosterol obtained from rape-seed oil is also a mixture, one constituent of which contains one double linking, whilst the other has two double linkings; these substances are very similar in properties to stigmasterol.

Stigmasterol acetate tetrabromide, $C_{32}H_{50}O_2Br_4$ (or $C_{32}H_{52}O_2Br_4$), is prepared by acetylating the crude phytosterol and then treating the ethereal solution of the dry acetate with a solution of bromine in acetic acid; the tetrabromide separates in small crystals, whilst the phytosterol acetate dibromide remains in solution. When recrystallised from a mixture of chloroform and alcohol it forms four- or six-sided plates, m. p. 211—212°. *Stigmasterol acetate* crystallises from alcohol in rectangular plates, m. p. 141°; a cryoscopic determination agrees with the formula $C_{32}H_{50}O_2$. The *propionate* crystallises from alcohol in prisms, m. p. 122°; the *propionate tetrabromide*, m. p. 202°, is similar to the corresponding derivative of the acetate. The *benzoate*, m. p. 160°, crystallises from a mixture of chloroform and alcohol in rectangular plates, the *chloride*, $C_{30}H_{47}Cl$ or $C_{30}H_{49}Cl$, from alcohol in prisms, m. p. 95°, and the *chloride tetrabromide* melts and decomposes at 180°.

W. R.

Transposition of Hydrobenzoin; Study of Alkylhydrobenzoins and some Trisubstituted Aromatic Glycols.

MARC TIFFENEAU and DORLENCOURT (*Compt. rend.*, 1906, 143, 1242—1244).—Aromatic trisubstituted glycols of the types $OH{\cdot}CHPh{\cdot}CRPh{\cdot}OH$ and $OH{\cdot}CHPh{\cdot}CRR{\cdot}OH$ yield the aldehydes $CHO{\cdot}CPh_2R$ and $CHO{\cdot}CPhR_2$ respectively, when treated with sulphuric acid and not the ketones as previously stated (Abstr., 1906, i, 724, 965). These trisubstituted (tertiary) aromatic aldehydes do not combine with alkali hydrogen sulphites or give a colour reaction with Schiff's reagent, but they are oxidised by silver oxide to form the corresponding acid, $CPh_2R{\cdot}CO_2H$ or $CPhR_2{\cdot}CO_2H$.

aa-Diphenylpropaldehyde, obtained by the action of sulphuric acid on methylhydrobenzoin, does not crystallise, b. p. 187—191°/22 mm., 174—178°/12 mm., or 301—304°/760 mm., $D^{0°}$ 1·087; the *oxime*, m. p. 123°, yields a *nitrile*, b. p. 310—313°; the *semicarbazone* has m. p. 122°.

aa-Diphenylpropionic acid, m. p. 173° (Thörmer and Zincke, Abstr., 1879, 322), is obtained when the aldehyde is oxidised by means of silver oxide; and the *oxide*, $C_{32}H_{34}O$, m. p. 121—122°, is prepared by the action of magnesium phenyl bromide.

aa-Diphenylbutaldehyde, obtained from ethylhydrobenzoin, has b. p. 312—316°, yields an *oxime*, m. p. 128—129°, and a *semicarbazone*, m. p.

167°, and is oxidised to *aa*-diphenylbutyric acid, m. p. 170—171° (Klingemann, Abstr., 1893, i, 590).

a-Phenyl-β-methylpropane-aβ-diol, $OH\cdot CHPh\cdot CMe_2\cdot OH$, m. p. 56°, obtained by the action of magnesium methyl iodide on methyl phenylglycollate, is converted by the action of sulphuric acid into *a-phenyl-a-methylpropaldehyde*, b. p. 105—110°/14 mm., which yields *a*-phenyl-*a*-methylpropionic acid on oxidation, and forms a *semicarbazone*, m. p. 176°.

a-Phenyl-β-ethylbutane-aβ-diol, m. p. 89°, b. p. 163—165°/20 mm. or 275—280°/760 mm., is partially converted by the action of sulphuric acid into *a-phenyl-a-ethylbutaldehyde*, b. p. 135—140°/26 mm. or 235—238°/760 mm., D^0 0·978, which forms a *semicarbazone*, m. p. 178—179°. M. A. W.

Application of the Grignard Reaction to Ethyl Aspartate. CARL PAAL and ERICH WEIDENKAFF (*Ber.*, 1906, **39**, 4344—4346. Compare Abstr., 1905, i, 436; 1906, i, 236, 583).—The reaction between ethyl ethyl-*i*-aspartate and excess of magnesium phenyl bromide in ether at 0°, leads to the formation of r-*β-amino-aaδδ-tetraphenylbutane-aδ-diol*, $OH\cdot CPh_2\cdot CH(NH_2)\cdot CH_2\cdot CPh_2\cdot OH$, m. p. 149—150°, which separates from dilute alcohol in white leaflets and forms sparingly soluble salts; the *hydrochloride* has m. p. 235°, and the *nitrate*, 168°. C. S.

The Six Isomeric Dinitrobenzoic Acids. ARNOLD F. HOLLEMAN and H. A. SIRKS (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 280—286).—When *m*-nitrotoluene is nitrated by nitric and sulphuric acids at 50°, 3:4-dinitrotoluene is obtained together with smaller quantities of 2:3-dinitrotoluene and of 3:6-dinitrotoluene; the three isomerides are separated by fractional distillation in a vacuum and freezing the distillate. The corrected solidifying points of the dinitrotoluenes of the benzoic esters and of their ethyl esters are tabulated; also D_4^{111} for the toluenes and the esters.

The dissociation constants and the velocity of esterification of the dinitrobenzoic acids have been measured with results in accordance with expectation; the dissociation constants cannot be calculated correctly from those of the monosubstituted acids by Ostwald's rule. For a detailed criticism of the results the original paper must be consulted. C. S.

Action of Nitrous Acid on *p*-Dimethylamino- and *p*-Diethylamino-benzoic Acids. OSKAR BAUDISCH (*Ber.*, 1906, **39**, 4293—4300).—The author has reinvestigated the action of nitrous acid on *p*-dimethylaminobenzoic acid, and, contrary to the statement of Bischoff (Abstr., 1889, 511), found it to lead to the formation of *p*-nitrodimethylaniline, *p*-nitrosomethylaminobenzoic acid, and *m*-nitro-*p*-dimethylaminobenzoic acid.

p-Nitrosomethylaminobenzoic acid, $NO\cdot NMe\cdot C_6H_4\cdot CO_2H$, crystallises from toluene or alcohol in glistening, straw-coloured needles, m. p. 217°, gives Liebermann's reaction, and when boiled with concentrated hydrochloric acid yields *p*-methylaminobenzoic acid, which is formed also by the action of methyl sulphate on *p*-aminobenzoic acid (Johnston, Proc., 1905, **21**, 156).

3-Nitro-4-dimethylaminobenzoic acid crystallises from toluene or chloroform in glistening, golden-yellow needles, m. p. 222—223°, does not give Liebermann's reaction, gives a red coloration changing through violet and bluish-green to dark red when reduced with zinc and hydrochloric acid and treated with ferric chloride, and forms a *hydrochloride* which is readily decomposed by water (compare Noelting and Demant, Abstr., 1904, i, 424).

The action of sodium nitrite on p-diethylaminobenzoic acid in hydrochloric acid solution leads to the formation of 4-nitrosoethylaminobenzoic acid, 4-nitronitrosoethylaniline, 3-nitro-4-ethylaminobenzoic acid, 3-nitro-4-diethylaminobenzoic acid, and 4-nitrodiethylaniline in amounts varying with the quantity of sodium nitrite and the concentration of the hydrochloric acid employed. The original must be consulted for the method of separating the products.

4-*Nitrosoethylaminobenzoic acid*, $NO\cdot NEt\cdot C_6H_4\cdot CO_2H$, crystallises from alcohol in glistening, straw-coloured needles, m. p. 193—194°, and gives Liebermann's reaction.

3-*Nitro*-4-*ethylaminobenzoic acid*, $NHEt\cdot C_6H_3(NO_2)\cdot CO_2H$, crystallises from light petroleum in glistening, golden-yellow needles, m. p. 239—240, forms a colourless *sulphate* which is readily decomposed by water, and when reduced with zinc and hydrochloric acid and treated with ferric chloride gives a dark red coloration, or with sodium nitrite a dark red, flocculent precipitate.

3-*Nitro*-4-*diethylaminobenzoic acid*, $NEt_2\cdot C_6H_3(NO_2)\cdot CO_2H$, crystallises from light petroleum in glistening, reddish-yellow needles, m. p. 117°, and gives a dark red coloration when reduced with zinc and hydrochloric acid and treated with ferric chloride. G. Y.

Action of Potassium Hypochlorite on Cinnamamide. R. A. Weerman (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 303—304).—When an alcoholic solution of cinnamamide (2 mols.) is treated with potassium hypochlorite (1 mol.), in which the free alkali has been neutralised just before use, a *carbamide*,

$$CHPh\colon CH\cdot NH\cdot CO\cdot NH\cdot CO\cdot CH\colon CHPh,$$

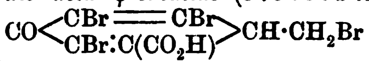
is obtained, which separates from glacial acetic acid in needles, m. p. 225—226°. C. S.

Hydroxytoluic Acids. I. 4-Hydroxy-*o*-toluic Acid. Theodor Zincke and H. Fischer (*Annalen*, 1906, **350**, 247—268. Compare Jacobson, Abstr., 1881, 599; Kalle & Co., D.R.-P. 81484, 91201; Einhorn, Abstr., 1900, i, 439).—The behaviour of 4-hydroxy-*o*-toluic acid towards bromine has been investigated from the point of view of its character as a derivative of *p*-cresol.

The action of bromine on 4-hydroxy-*o*-toluic acid with or without glacial acetic acid as solvent, at the laboratory temperature, and finally at 60—65°, leads to the formation of 3 : 5-*dibromo*-4-*hydroxy*-*o*-*toluic acid*, $OH\cdot C_6HMeBr_2\cdot CO_2H$, which crystallises from benzene in slender needles, from acetic acid in stout needles, m. p. 141°, and forms a white, crystalline *silver* salt. The *acetyl* derivative crystallises in slender needles, m. p. 125°; the *methyl ester* forms long white needles, m. p. 108—109°.

A monobromo-4-hydroxy-*o*-toluic acid cannot be obtained, a part of the acid remaining unchanged when insufficient bromine for the formation of the dibromo-derivative is employed.

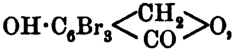
3 : 5 : 6-*Tribromo-4-hydroxy-o-toluic acid,* $OH\cdot CMeBr_3\cdot CO_2H$, prepared by heating 4-hydroxy-*o*-toluic acid or its dibromo-derivative with bromine on the water-bath, crystallises from hot benzene or water in glistening needles, m. p. 193—194°, decomposes slowly on prolonged boiling with aqueous sodium carbonate, forms a *silver* salt which blackens on exposure to air, and is converted by concentrated nitric acid into a *bromodinitro-acid,* crystallising in long needles, and commencing to decompose at 200°. The *acetyl* derivative of the tribromo-acid crystallises in short, monoclinic prisms, m. p. 176°.

3 : 5 : 6-*Tribromo-4-hydroxy-*o*-toluic acid ψ-bromide* (3 : 5 : 6 : *ω-tetrabromo-4-hydroxy-*o*-toluic acid*),  $CO<\begin{matrix}CBr{=\!=}CBr\\ CBr{:}C(CO_2H)\end{matrix}>CH\cdot CH_2Br$ or $OH\cdot C_6Br_3(CO_2H)\cdot CH_2Br$, formed by heating the tribromo-acid with an excess of bromine in a sealed tube at 120—125°, crystallises in long, white needles, m. p. 168°, and when treated with acetic anhydride and concentrated sulphuric acid, yields an *acetyl* derivative, $OAc\cdot C_6Br_3(CO_2H)\cdot CH_2Br$; this crystallises in stout, glistening needles, m. p. 198—199°, and is converted by aqueous sodium carbonate into *tribromo-4-hydroxyphthalide.*

When treated with methyl alcohol and concentrated sulphuric acid, the tetrabromo-acid yields 3 : 5 : 6-*tribromo-4-hydroxy-ω-methoxy-o-toluic acid,* $OH\cdot C_6Br_3(CO_2H)\cdot CH_2\cdot OMe$, which crystallises from benzene in stout, colourless needles, m. p. 145—146°, or from dilute acetic acid in glistening prisms containing H_2O, m. p. 114—115°; it dissolves unchanged in aqueous sodium carbonate, and is converted by acetic anhydride and sulphuric acid into the *acetyl* derivative of the phthalide.

The action of boiling acetic anhydride and sodium acetate on the tetrabromo-acid leads to the formation of the phthalide and a sandy, sparingly soluble *substance,* m. p. above 260°, which is formed also on heating the tribromomethoxy-acid above its melting point.

Tetrabromo-4-hydroxy-o-toluic acid perbromide, $(C_8H_4O_3Br_4)_2Br_2$, prepared by heating the tetrabromo-acid with an excess of bromine at 135—140° or with bromine in carbon tetrachloride solution, forms glistening, red needles, is moderately stable at the laboratory temperature, is decolorised by acetone, sodium hydrogen sulphite, or sodium hydroxide, and yields the tetrabromo-acid when heated, when dissolved in ether, or when boiled with benzene.

3 : 5 : 6-*Tribromo-4-hydroxyphthalide,*  $OH\cdot C_6Br_3<\begin{matrix}CH_2\\ CO\end{matrix}>O$, prepared by the action of 10% sodium carbonate solution on the tetrabromo-acid or by boiling the acid with aqueous acetone, crystallises in glistening needles, m. p. 207°, remains unchanged when heated with hydrogen bromide or with aniline, and forms a *sodium* salt crystallising in long, white needles. The *acetyl* derivative crystallising in glistening needles, m. p. 222—223°.

Tribromo-4-hydroxyphthalideanil, $OH\cdot C_6Br_3<\substack{CH_2 \\ CO}>NPh$, formed by the action of aniline on tetrabromo-4-hydroxy-*o*-toluic acid, crystallises in glistening needles, m. p. 220°; the *acetyl* derivative, $C_{16}H_{10}O_3NBr_3$, forms broad, glistening needles, m. p. 225—226°.

The nitro-4-hydroxy-*o*-toluic acids formed by nitration of 4-hydroxy-*o*-toluic acid (Einhorn, *loc. cit.*) are separated by boiling with methyl-alcoholic hydrogen chloride, when 3-nitro-4-hydroxy-*o*-toluic acid, m. p. 197°, remains unchanged, whilst 5-nitro-4-hydroxy-*o*-toluic acid, m. p. 160°, is converted into its *methyl* ester, $C_9H_9O_5N$, crystallising in yellow leaflets, m. p. 99°. 3-*Nitro*-4-*acetoxy*-o-*toluic acid*, forms long, broad, almost colourless leaflets, m. p. 139—140°.

5-*Bromo*-3-*nitro*-4-*hydroxy*-o-*toluic acid*, $OH\cdot C_6HMeBr(NO_2)\cdot CO_2H$, formed by the action of nitric acid or sodium nitrite on 3:5-dibromo-4-hydroxy-*o*-toluic acid or by the nitration of 3-nitro-4-hydroxy-*o*-toluic acid, crystallises in stout, yellow needles, m. p. 208°, forms characteristic *ammonium*, *sodium*, *barium*, and *silver* salts, and is reduced by tin and hydrogen chloride in methyl alcoholic solution, forming 5-bromo-3-amino-*p*-cresol, or by zinc dust in neutral solution, or by alkali sulphides, forming 5-*bromo*-3-*amino*-4-*hydroxy*-o-*toluic acid*,

$$OH\cdot C_6HMeBr(NH_2)\cdot CO_2H.$$

This crystallises in colourless needles, m. p. 179—180°, becomes brown on exposure to air in alkaline solution, and yields a sparingly soluble *diazo*-derivative. The *diacetyl* derivative, $C_{12}H_{11}O_5NBr$, crystallises in long needles, m. p. 189—190°. G. Y.

Tyrosamines. Armand Gautier (*Bull. Soc. chim.*, 1906, [iii], **35**, 1195—1197).—Water extracts from codfish livers, which have been allowed to ferment spontaneously, a mixture of amylamine and like substances with three *bases* represented by the formulæ C_7H_9ON, $C_8H_{11}ON$, and $C_9H_{13}ON$, which form colourless needles or lamellæ, and when heated at 220° sublime slightly and decompose. They are bitter, possess a slight, non-ammoniacal odour, are alkaline to test-paper, and give all the characteristic colour reactions of tyrosine. It is suggested that these bases are derived from tyrosine and its next two lower homologues by the loss of a molecule of carbon dioxide. The most abundant of the three bases is that having the formula $C_8H_{11}ON$, which on the above assumption is *p*-hydroxyphenylethylamine. It is soluble in 95 parts of water at 15°, crystallises in the cold, but blackens by oxidation on exposure to air. Its salts are neutral and bitter, the *hydrochloride* and *sulphate* form hygroscopic spangles or needles, and the *platinichloride* is yellow and readily soluble. All three tyrosamines are but slightly toxic. Similar products have been obtained by Leger (Abstr., 1906, i, 204, 761) and by Brieger. T. A. H.

Isomerism of Ethylcoumaric and Ethylcoumarinic Acids. Arthur Michael and Arthur B. Lamb (*Amer. Chem. J.*, 1906, **36**, 552—580).—The question whether coumaric and coumarinic acids are spacial or structural isomerides has not been conclusively decided, but spacial modifications of the hydroxycinnamic acids are undoubtedly capable of existence. Cinnamic acid is changed into *allo*cinnamic acid by converting it into phenylpropiolic acid, adding hydrogen bromide to this, and reducing the bromocinnamic acid thus obtained. A similar series of operations with ethylcoumaric acid is found to yield ethylcoumarinic acid, an observation which argues strongly that the relation between these acids is similar to that existing between the stereoisomeric cinnamic acids.

In the reduction of β-bromo-*o*-ethoxy*allo*cinnamic acid no indications are given of the formation of an acid corresponding with *iso*cinnamic acid.

The method given by Ebert (Abstr., 1883, 471) for the preparation of ethylcoumarinic acid from coumarin, an absolute alcoholic solution of sodium ethoxide and ethyl iodide, gives the isomeric ethylcoumaric acid; if, however, the absolute alcohol is replaced by 96% alcohol, a good yield of ethylcoumarinic acid is obtained. Ebert's conclusion (*loc. cit.*) that the addition of bromine to ethylcoumaric and to ethylcoumarinic acid yields the same dibromide is confirmed.

Using the method given by Claus (*Annalen*, 1892, **269**, 2) for the preparation of ethoxyphenylpropiolic acid, the authors were unable to obtain an acid free from traces of halogen, which could only be removed by conversion of the acid into the calcium salt, followed by digestion with 50—60% alcohol and reconversion into the acid. The acid obtained in this way has m. p. 115·5—116°; Ebert gave 114°.

The action of hydrobromic acid on ethoxyphenylpropiolic acid yields: (1) ethylbromocoumaric acid, m. p. 120°, with the bromine atom in the β-position to the carboxyl group; (2) a small proportion of an *acid*, $C_{10}H_{11}O_3$, crystallising from a mixture of acetone and light petroleum in white needles, m. p. 211—212·5°.

The reduction of β-bromo*allo*cinnamic acid in alcoholic solution by means of zinc dust yields mainly *allo*cinnamic acid, together with cinnamic acid and an acid with a very low melting point. When reduced in this way, bromo-β-ethylcoumaric acid is converted almost entirely into ethylcoumarinic acid, the proportion of ethylcoumaric acid yielded being small; ethylmellilotic acid could not be detected among the products of the reduction and cannot be formed in other than very minute quantities.

aβ-Dibromo-β-bromoethoxyphenylpropionic acid,

$$OEt\cdot C_6H_3Br\cdot C_2H_2Br_2\cdot CO_2H,$$

prepared by the action of bromine (4 atoms) on ethylcoumarinic acid in chloroform solution, separates from toluene in colourless, rectangular crystals, and from a mixture of acetone and light petroleum in short, slightly rhombic needles, m. p. 182—183° (decomp.).

The action of bromine (4 atoms) on ethylcoumaric acid yields a gummy residue which, when dissolved in alcohol and treated with sodium hydroxide and the solution acidified, gives *bromo-*o*-ethoxyphenylpropiolic acid*, $OEt\cdot C_6H_3Br\cdot C{:}C\cdot CO_2H$, crystallising in needles, m. p. 134—136°. The gummy residue hence consists principally of a tribromo-derivative of ethylcoumaric acid or of bromo *o*-ethoxyphenyldibromopropionic acid. This evidence of the dissimilarity of the corresponding products derived from ethylcoumarinic and ethylcoumaric acids requires confirmation, since Perkin found that the two methyl acids gave the same bromo-*o*-methoxyphenyldibromopropionic acid.

The action of bromine vapour in excess on ethylcoumaric acid yields *αβ-dibromo-β-dibromoethoxyphenylpropionic acid*,

$$OEt \cdot C_6H_2Br_2 \cdot C_2H_2Br_2 \cdot CO_2H,$$

which crystallises from toluene or light petroleum in thin, rhombic plates, m. p. 183—184°. Ethylcoumarinic acid probably yields the same acid, but the product could not be purified.

When treated with a solution of chlorine in carbon tetrachloride, ethylcoumarinic acid yields the *compound*, $OEt \cdot C_6H_4 \cdot C_2H_2Cl \cdot CO_2H$, which separates from light petroleum in crystals, m. p. 130—131°.

Ethylcoumarinic acid is not acted on by alcoholic solution of sodium ethoxide, but heating with dilute mineral acid converts it into ethylcoumaric acid (compare Perkin, Trans., 1877, **31**, 388), as also does treatment with iodine in carbon disulphide solution. T. H. P.

Replacement of the Hydroxyl of some Carbinols by the Group $-CH_2 \cdot CO_2H$.

Robert Fosse (*Compt. rend.*, 1906, **143**, 914—916).—ββ-Disubstituted propionic acids are readily obtained by the condensation of malonic acid and secondary aromatic carbinols which contain the group $-OMe$, $:O_2:CH_2$ or $-NMe_2$, according to the equation $:CH \cdot OH + CH_2(CO_2H)_2 = H_2O + CO_2 + :CH \cdot CH_2 \cdot CO_2H$, and the following acids were thus prepared: (1) *β-phenyl-β-*p*-methoxyphenylpropionic acid*, $OMe \cdot C_6H_4 \cdot CHPh \cdot CH_2 \cdot CO_2H$, m. p. 121·5—122·5°; (2) *β-*p*-methoxyphenyl-β-α-naphthylpropionic acid*,

$$OMe \cdot C_6H_4 \cdot CH(C_{10}H_7) \cdot CH_2 \cdot CO_2H,$$

and its p-*toluidide*, $OMe \cdot C_6H_4 \cdot CH(C_{10}H_7) \cdot CH_2 \cdot CO \cdot NH \cdot C_7H_7$, melts at 176—177°; (3) *β-phenyl-β-3:4-dioxymethylenephenylpropionic acid*, $CH_2O_2:C_6H_3 \cdot CHPh \cdot CH_2 \cdot CO_2H$, m. p. 155—156°; (4) *β-3:4-dioxymethylenephenyl-β-α-naphthylpropionic acid*,

$$CH_2O_2:C_6H_3 \cdot CH(C_{10}H_7) \cdot CH_2 \cdot CO_2H,$$

m. p. 205°; (5) β-3:4-dioxymethylenephenyl-β-*p*-tolylpropionic acid, $CH_2O_2:C_6H_3 \cdot CH(C_7H_7) \cdot CH_2 \cdot CO_2H$, m. p. 161°; (6) *β-phenyl-β-*p*-dimethylaminophenylpropionic acid*, $NMe_2 \cdot C_6H_4 \cdot CHPh \cdot CH_2 \cdot CO_2H$, m. p. 184·5°; (7) *β-*p*-dimethylaminophenyl-β-α-naphthylpropionic acid*, $NMe_2 \cdot C_6H_4 \cdot CH(C_{10}H_7) \cdot CH_2 \cdot CO_2H$, m. p. 183°, the *silver*, *lead*, and *calcium* salts have been prepared; (8) *ββ-di-*p*-dimethylaminophenylpropionic acid*, $CH(C_6H_4 \cdot NMe_2)_2 \cdot CH_2 \cdot CO_2H$, m. p. 222—230°, the *potassium*, *sodium*, *calcium*, *lead*, *barium*, and *silver* salts have been prepared. Most of the acids described form white, amorphous silver salts. M. A. W.

Nitration of Phthalic Acid and of *iso*Phthalic Acid.

Arnold F. Holleman and J. Huisinga (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, **9**, 286—292).—5-Nitro*iso*phthalic acid, obtained by nitrating *iso*phthalic acid, crystallises with $1H_2O$, and has m. p. 255—256°.

4-Nitro*iso*phthalic acid is obtained by oxidising the corresponding xylene, prepared by nitrating xylene at 0° with nitric acid of D 1·48, with an alkaline solution of potassium permanganate. It has m. p. 245°.

2-Nitro*iso*phthalic acid, obtained by oxidising the corresponding nitroxylene, crystallises in needles, m. p. 300°.

The quantitative nitration of phthalic acid requires three weeks at 30°, and yields 49·5% of α- and 50·5% of β-nitrophthalic acids. Under similar conditions, *iso*phthalic acid yields 96·9% of the 5-nitro- and 3·1°/₀ of the 4-nitro*iso*phthalic acids, the proportions being ascertained by solubility determinations. C. S.

Santonin. EDGAR WEDEKIND (*Arch. Pharm.*, 1906, **244**, 623—639).—The oxonium salts of santonin (compare Abstr., 1905, i, 211) with ferrocyanic and ferricyanic acids, $C_{15}H_{18}O_3,H_4Fe(CN)_6$ and $C_{15}H_{18}O_3,H_3Fe(CN)_6$ respectively, were analysed; the cobalticyanide, which is distinctly crystalline, was not analysed.

A *sodium santoninsulphonate*, $C_{15}H_{17}O_3 \cdot SO_3Na$, $[\alpha]_D^{20} - 10{\cdot}25°$, was obtained by heating chlorosantonin (Abstr., 1905, i, 212, 529) with aqueous sodium sulphite for several hours at 140—150°; the purest sample prepared contained 96·5°/₀. The substance is not a vermifuge.

With hydroxylamine, santonin yields a product, m. p. 92—96°, which contains *N* 9·3°/₀, corresponding approximately with two atoms of nitrogen in the molecule. The substance is not a dioxime, however, for when it is heated with dilute mineral acids it yields, not santonin, but a resinous product which contains nitrogen.

Concentrated hydrochloric acid, either at the ordinary temperature or at 60°, converts santonic acid partially into desmotroposantonin.

The paper contains a short statement of the modern views of the constitution of santonin and of some of its derivatives. C. F. B.

Action of Light on Oximes. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 721—728. Compare Ciamician and Silber, Abstr., 1904, i, 161).—The author confirms Goldschmidt's observation (Abstr., 1904, i, 250) that the oxime, m. p. 121—122°, obtained directly from *m*-nitrobenzaldehyde is the *anti*-oxime, which, when transformed by the Beckmann method, yields the *syn*-oxime, m. p. 118—119°.

The oximes of *m*-nitroanisaldehyde and *p*-chlorobenzaldoxime behave normally towards light and are transformed into the corresponding *syn*-oximes. *anti*-Benzaldoxime and *anti*-piperonaldoxime, however, remain unchanged, so that the presence of a negative group in the molecule of the aldehyde appears necessary for the passage from the *anti*- to the *syn*-oxime.

syn-Benzaldoxime is converted almost entirely into the *anti*-oxime on exposure to light, but with *syn*-*m*-nitrobenzaldoxime, 53% remains unchanged after six months.

m-Nitroanisaldehyde, prepared by Wörner's method (Abstr., 1896, i, 225), has m. p. 86—87°. Its p-*nitrophenylhydrazone*,

$$NO_2 \cdot C_6H_3(OMe) \cdot CH{:}N_2H \cdot C_6H_4 \cdot NO_2,$$

separates from a mixture of alcohol and acetone in yellow crystals, m. p. 244°. The *oxime*, $NO_2 \cdot C_6H_3(OMe) \cdot CH{:}NOH$, is deposited from alcohol in silky, white, acicular crystals, m. p. 170°. The syn-*oxime*, prepared by Beckmann's method, crystallises from benzene in faintly yellow needles, m. p. 168—170°. The *benzyl* derivative of the *anti*-

oxime, $NO_2 \cdot C_6H_3(OMe) \cdot CH{:}NO \cdot CH_2Ph$, separates from alcohol in shining, white needles, m. p. 124°, and the corresponding syn-*derivative* crystallises from alcohol in slender, yellow needles, m. p. 195°.

anti-p-Chlorobenzaldoxime, has m. p. 110°, and the *syn*-compound, m. p. 146° (compare Erdmann and Schwechten, Abstr., 1891, 448).

T. H. P.

Methyl *p*-Tolyl Ketone. Carl Thomae and Hermann Lehr (*Arch. Pharm.*, 1906, **244**, 651—652).—Some details are given of the preparation of this ketone from acetyl chloride, toluene, and aluminium chloride, and carbon disulphide (?) (Claus and Riedel, Abstr., 1886, 642).

C. F. B.

Compounds of Ketones with Ammonia. Carl Thomae (*Arch. Pharm.*, 1906, **244**, 641—642. Compare Abstr., 1905, i, 509, also 684, 718).—A paper introductory to those with which the following two abstracts deal. Ketone ammonias are hydrolysed readily to ketones and ammonia by dilute aqueous acids. Alcoholic picric acid removes NH_3, forming *monoazo-ketone ammonias*; when these are distilled they lose 1 mol. of a hydrocarbon, aliphatic or aromatic, yielding trialkyl derivatives of pyridine, which sometimes can be obtained directly from the ketones by heating these strongly with alcoholic ammonia in closed vessels. The yields obtained from the ketones are small, amounting to but a few per cents. of the theoretical ones.

C. F. B.

Compounds of Ketones with Ammonia. Action of Ammonia on Acetophenone. Carl Thomae (*Arch. Pharm.*, 1906, **244**, 643—651).—The crude product of the action of ammonia on acetophenone at the ordinary temperature, after spontaneous evaporation of the ammonia and of most of the alcohol, was diluted with ether, mixed with coarsely powdered ice, and shaken with a slight excess of dilute (1 : 9) hydrochloric acid; from the ethereal solution, which contains much unaltered acetophenone, acetophenone ammonia hydrochloride separates. This was suspended in much alcohol, and the mixture was shaken with solid potassium hydroxide until the reaction was faintly alkaline; the liquid was filtered and the alcohol allowed to evaporate at the ordinary temperature; the residue was stirred with a little alcohol, and the crystals drained, and recrystallised from alcohol; the yield was small.

Thus obtained, *acetophenone ammonia*, $CMePh(N{:}CMePh)_2$ or $C_{24}H_{24}N_2$ (molecular weight determined ebullioscopically in benzene), has m. p. 115°; it reacts like a tertiary base with benzenesulphonyl chloride. It is not decomposed rapidly by water, but if a few drops of hydrochloric acid are added, hydrolysis to acetophenone and ammonia begins at once; in consequence the hydrochloride was not obtained in the pure state, nor could a platinichloride be prepared.

With picric acid in alcoholic solution, acetophenone ammonia yields yellow *monoazo-acetophenone ammonia picrate*, $C_{24}H_{21}N,C_6H_3O_7N_3$, elimination of NH_3 taking place; this melts at 210·5°. The corresponding hydrochloride is present in the aqueous portion of the aqueous-ethereal mixture from which the acetophenone ammonia hydrochloride separated. The base is formed in larger yield when an alcoholic solution of acetophenone is saturated with ammonia in the cold and then heated at 150—180° for twenty-seven hours in sealed glass tubes (under these circumstances no acetophenone ammonia is formed); it was only obtained in an oily or pasty condition.

When crude monoazo-acetophenone ammonia is distilled, it yields triphenylpyridine (acetophenine), $C_{23}H_{17}N$, with elimination of CH_4.

From the ethereal portion of the aqueous-ethereal mixture already mentioned (which contains much unchanged acetophenone), a crystalline substance of another type, containing no nitrogen, was obtained by distillation; it is undergoing investigation. C. F. B.

Compounds of Ketones with Ammonia. Action of Ammonia on Methyl *p*-Tolyl Ketone. CARL THOMAE and HERMANN LEHR (*Arch. Pharm.*, 1906, **244**, 653—664).—The method of manipulation and the products obtained were of a similar character to those in the case of acetophenone (compare preceding abstract).

Methyl p-*tolyl ketone ammonia*, $C_6H_4Me\cdot CMe(N\colon CMe\cdot C_6H_4Me)_2$ or $C_{27}H_{30}N_2$ (molecular weight determined ebullioscopically in benzene), has m. p. 111°; the *platinichloride*, $C_{27}H_{30}N_2,H_2PtCl_6$, has m. p. 203—204°.

Monoazo-methyl p-*tolyl ketone ammonia picrate*, $C_{27}H_{27}N,C_6H_3O_7N_3$, has m. p. 211°. The base is not formed in appreciable quantity when the ketone is heated strongly with alcoholic ammonia.

In these circumstances, *methylditolylpyridine*, $C_{20}H_{19}N$ (molecular weight determined ebullioscopically in benzene), is formed, corresponding with elimination of NH_3 and C_6H_5Me from the ketone ammonia; it has m. p. 97·5°; the *picrate*, $C_{20}H_{19}N,C_6H_3O_7N_3$, m. p. 211°, is hydrolysed by water, as also is the chloride. A small quantity of a substance of m. p. 176° was also obtained; possibly this was tritolylpyridine, resulting from elimination of NH_3 and CH_4 from the ketone ammonia.

A crystalline product free from nitrogen was obtained, as in the case of acetophenone. C. F. B.

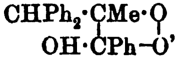
Reaction Between Unsaturated Compounds and Organo-Magnesium Compounds. X. Reactions with α-Methylcinnamic Acid. ELMER P. KOHLER (*Amer. Chem. J.*, 1906, **36**, 529—538. Compare Abstr., 1906, i, 753).—The author has studied the interactions between α-methylcinnamic acid and organo-magnesium compounds in order to determine the influence exerted on the action by a "positive" group in the α-position of unsaturated esters. The results obtained with benzylidenepropiophenone are exactly analogous with those yielded by benzylideneacetophenone (Abstr., 1904, i, 595).

The results given in the present paper show that Blaise and Courtot's interpretation of the course of the reaction between Grignard's reagent and methylacrylic acid (Abstr., 1905, i, 257) as a direct union of the reagent to the double linking between carbon atoms is erroneous. The formation of a certain amount of saturated ketone in the action between the methylacrylic acid and magnesium methyl iodide is due to αδ-addition, thus: (1) $CH_2\colon CMe\cdot CO_2Et + MgMeI = CH_2\colon CMe\cdot COMe + MgI\cdot OEt$; (2) $CH_2\colon CMe\cdot COMe + MgMeI = CMeEt\colon CMe\cdot O\cdot MgI$ and this $+ H_2O = CMeEt\colon CMe\cdot OH = CHMeEt\cdot COMe$.

The first action between methyl α-methylcinnamate and an organo-magnesium derivative invariably consists in the replacement of methoxyl by a hydrocarbon residue, an unsaturated ketone being formed. When an excess of the reagent is present, the unsaturated ketone reacts immediately with a second molecule, forming either the magnesium derivative of a tertiary alcohol by addition to carbonyl or the derivative of an unsaturated alcohol by αδ-addition. When the magnesium derivative is carefully decomposed with iced acid, the resulting ethereal solution, on heating, gives only an unsaturated ketone, but when it is evaporated at a low temperature in a stream of moist air or oxygen, a peroxide is formed. This behaviour is peculiar to unsaturated alcohols obtained by αδ addition to ketones with a hydrocarbon residue in the α-position.

αγγ-Triphenyl-β-methylpropenyl benzoate, $OBz\cdot CPh\colon CMe\cdot CHPh_2$, prepared by the action of benzoyl chloride on the intermediate magnesium derivative obtained in the interaction of magnesium phenyl bromide and methyl α-methylcinnamate, crystallises from a mixture of chloroform and alcohol in needles, m. p. 122°.

α-Bromo-ββ-diphenyl-α-methylpropiophenone, $CHPh_2\cdot CBrMe\cdot COPh$, prepared by the action of bromine on the magnesium derivative of triphenylmethylpropenol, crystallises from a mixture of ether and light petroleum in large, lustrous plates, m. p. 93°.

αγγ-Triphenyl-β-methylpropenol peroxide, 
$\begin{array}{l} CHPh_2\cdot CMe\cdot O \\ \qquad\quad | \qquad\ | \\ \quad OH\cdot CPh-O \end{array}$, crystallises from a mixture of ether and light petroleum in colourless needles, m. p. 127°, has the normal molecular weight in boiling ethyl ether, and, when pure, is stable at the ordinary temperature. When heated on a steam-bath or melted, it explodes, giving benzoic acid, *s*-tetraphenylethane, and a small proportion of diphenylmethane, the first two of these products being also obtained on warming the peroxide with concentrated alcoholic potassium hydroxide. If, however, the peroxide is added slowly to cooled, dilute, alcoholic potassium hydroxide, it yields the intermediate *α-hydroxy-ββ-diphenyl-α-methylpropiophenone*, $CHPh_2\cdot CMe(OH)\cdot COPh$, which crystallises from a mixture of acetone and alcohol in colourless plates, m. p. 188°, has the normal molecular weight in boiling ether, and is also obtained when dilute potassium hydroxide solution is gradually added to a cooled solution of α-bromo-ββ-diphenyl-α-methylpropiophenone.

Methyl α-methylcinnamate reacts with 2 mols. of magnesium methyl iodide, even when the latter is slowly added to excess of the ester, the product being *α-phenyl-βγ-dimethylbutadiene*,

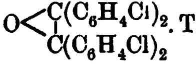
$$CHPh\colon CMe\colon CMe\colon CH_2,$$

b. p. 165°/30 mm.

T. H. P.

Intramolecular Atomic Transpositions. IV. Aromatic Oximes. P. J. MONTAGNE (*Rec. trav. chim.*, 1906, 25, 376—378. Compare Abstr., 1905, i, 445).—The fact that 4 : 4′-dichlorobenzophenone after undergoing the Beckmann transformation yields on hydrolysis *p*-chlorobenzoic acid and *p*-chloroaniline shows that the rearrangement does not involve any change in the point of attachment of the ketonic carbon atom to the aromatic nucleus. P. H.

Intramolecular Atomic Transpositions. V. Conversion of 4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacolin into *s*-4 : 4′ : 4″ : 4‴-Tetraphenylethane. P. J. MONTAGNE (*Rec. trav. chim.*, 1906, **25**, 379—410. Compare Abstr., 1905, i, 58, 445, 524).—The theory put forward by Klinger and Lonnes (Abstr., 1896, i, 691, 692) to explain the transformation of β-benzopinacolin into *s*-tetraphenylethane, first described by Thörner and Zincke (Abstr., 1878, 425), necessitates a change in the carbon atom by which the aromatic nucleus is attached. The results obtained in the present communication refute this theory, since there is no alteration in the positions of the chlorine atoms when 4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacolin is converted into 4 : 4′ : 4″ : 4‴-tetrachlorotetraphenylethane. In the interaction of 4 : 4′-dichlorobenzophenone with *p*-chlorobenzoyl chloride in the presence of aluminium chloride (Abstr., 1902, i, 472) the yield, which in bright daylight is 75—80%, may be increased to 90% or more in the presence of direct sunlight; in addition to 4 : 4′-dichlorobenzophenone some 2 : 4′-dichlorobenzophenone is formed, thus disproving Beilstein's rule that only para-substituted derivatives are formed during a Friedel and Craft condensation. 4 : 4′-*Dichlorodiphenylmethane,* obtained by reducing 4 : 4′-dichlorodiphenylmethane with hydriodic acid and amorphous phosphorus, crystallises from light petroleum in large, flattened, monoclinic crystals [$a : b : c = 1·8365 : 1 : 1·6586$; $\beta = 88°45′$], m. p. 55°. 4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacone (Abstr., 1905, i, 445) can in the absence of sunlight be prepared by reducing dichlorobenzophenone with zinc and sulphuric acid. The reduction of 4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacolin with hydriodic acid and amorphous phosphorus yields in addition to 4 : 4′ : 4″ : 4‴-tetrachlorotetraphenylethane a substance of the molecular formula $C_{26}H_{18}Cl_4$, which crystallises from light petroleum in slender needles, m. p. 215·5°, or from benzene in triclinic prisms, $C_{26}H_{18}Cl_4,2C_6H_6$ [$a:b:c = 1·0792 : 1 : 0·9831$; $\alpha = 131°54′$; $\beta = 118°50\frac{2}{3}′$; $\gamma = 74°41\frac{1}{2}′$]. A quantitative yield of diphenylcarbinol was obtained by adding successively 25 grams of benzophenone and 30 grams of zinc powder to a boiling solution of 25 grams of potassium hydroxide in 200 c.c. of pure alcohol. P. H.

Intramolecular Atomic Transpositions. VI. Conversion of α-4 : 4′ : 4″ : 4‴-Tetrachlorobenzopinacolin into the β-Variety. P. J. MONTAGNE (*Rec. trav. chim.*, 1906, **25**, 411—414. Compare Abstr., 1905, i, 58, 445—524).—On reducing 4 : 4′-dichlorobenzophenone by means of zinc dust and acetic acid in presence of dilute sulphuric acid for eight days, only a very small quantity of 4 : 4′-dichlorodiphenylcarbinol is obtained, the main product of the reaction being 4 : 4′-dichlorodiphenylmethane and α-4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacolin,  $O<\begin{matrix}C(C_6H_4Cl)_2\\|\\C(C_6H_4Cl)_2\end{matrix}$. The latter crystallises from light petroleum in small needles, m. p. 235° (decomp.). On oxidation with chromic acid it yields 4 : 4'-dichlorobenzophenone, and when heated with acetyl chloride at 100° it is converted into β-4 : 4' : 4'' : 4'''-tetrachlorobenzopinacolin, $C(C_6H_4Cl)_3{\cdot}CO{\cdot}C_6H_4Cl$; boiling alcoholic potassium hydroxide breaks it up into *p*-chlorobenzoic acid and 4 : 4' : 4''-trichlorotriphenylmethane, showing that during the migration of the group C_6H_4Cl-, necessitated by the change from the α- to the β-variety, the relative position of the chloride atom has not been altered, and accordingly that the aromatic nucleus must be attached by the same carbon atom both before and after the transposition. P. H.

The Alkaline Reduction of *p*- and *m*-Nitrobenzophenones. Paul Carré (*Compt. rend.*, 1907, **144**, 34—35).—The *m*- and *p*-nitrobenzophenones were prepared by the condensation of the corresponding nitrobenzoyl chlorides with benzene in the presence of aluminium chloride. m-*Nitrobenzophenonephenylhydrazone* crystallises in yellow needles, m. p. 116°; the corresponding p-*nitro*-compound forms small, reddish-orange crystals, m. p. 142°. *p*-Nitrobenzophenone, when boiled with zinc and alcoholic soda, gives first a mixture of azo- and azoxybenzophenone which cannot be separated. By continued reduction, the ketonic group is attacked. Reduction of this mixture with ammonium hydrosulphide gives p-*hydrazobenzophenone*,

$$COPh{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}COPh,$$

which crystallises with H_2O in white needles, m. p. 130°; the anhydrous substance has m. p. 162°. On oxidation with mercuric oxide it gives p-*azobenzophenone*, $N_2(C_6H_4{\cdot}COPh)_2$, which forms red lamellæ, m. p. 219°. The *phenylhydrazone* forms small, bright red crystals, m. p. 130°. *m*-Nitrobenzophenone gives by similar reduction *m*-azoxybenzophenone (Elbs and Wogrinz, Abstr., 1903, i, 635). Ammonium hydrosulphide reduces this to an oily compound which cannot be purified and is oxidised by mercuric oxide to *m*-azobenzophenone (Elbs and Wogrinz, *loc. cit.*). Continued reduction of the *m*-azoxybenzophenone results in the attack of the ketonic group and the breaking up of the molecule. The results are analogous to those observed in the reduction of *m*- and *p*-nitrobenzyl alcohols (Abstr., 1905, i, 889). E. H.

***o*-Aminobenzophenone Derivatives.** Fritz Ullmann and Walter Denzler (*Ber.*, 1906, **39**, 4332—4339. Compare Abstr., 1903, i, 176).—The authors have prepared a series of *o*-aminomethoxybenzophenones by condensing arylsulphoneanthranilic chlorides with the methyl ethers of the three dihydroxy-benzenes, pyrogallol, and the two naphthols respectively. The behaviour of the resulting *o*-aminoketones on diazotisation is also described.

p-*Toluenesulphone-2-amino-2'- : 5'-dimethoxybenzophenone*,

$$C_7H_7{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3{\cdot}(OMe)_2,$$

obtained by the addition of quinol dimethyl ether and aluminium chloride to *p*-toluenesulphoneanthranilic chloride, crystallises in colourless leaflets, m. p. 156°. When warmed with a mixture of equal parts of concentrated sulphuric acid and glacial acetic acid, it forms 2-*amino*-2' : 5'-*dimethoxybenzophenone*, $C_{15}H_{15}O_3N$, which separates from a mixture of ether and light petroleum in amber-coloured crystals, m. p. 98°. When the latter compound is diazotised and the resulting solution heated, 2-methoxyxanthone, m. p. 131°, is obtained, which is converted into 2-hydroxyxanthone when warmed with aluminium chloride.

p-*Toluenesulphone-2-amino-2′ : 4′-dimethoxybenzophenone*, obtained from resorcinol in similar manner, separates from a mixture of benzene and light petroleum in glistening needles, m. p. 139°. On saponification it forms 2-*amino-2 : 4′-dimethoxybenzophenone*, which crystallises in yellow, stellate needles, m. p. 128°. When diazotised, as in the preceding case, it forms 3-methoxyxanthone, which is readily converted into 3-hydroxyxanthone.

p-*Toluenesulphone-2-amino-3 : 4′-dimethoxybenzophenone*, obtained from veratrol, has m. p. 125° and resembles its isomerides. It forms 2-*amino-3′ : 4′-dimethoxybenzophenone*, which separates from a mixture of benzene and light petroleum in yellow needles, m. p. 74°, and, when diazotised, forms a mixture of *dimethoxyfluorenone*, $C_{15}H_{12}O_3$, m. p. 164°, and 2-hydroxy-3′-4′-dimethoxybenzophenone.

p-*Toluenesulphone-2-amino-2′ : 3′ : 4′-trimethoxybenzophenone*,

$C_{23}H_{23}O_6NS$,

obtained by the condensation of pyrogallol trimethyl ether with *p*-toluenesulphoneanthranilic chloride, separates from alcohol in colourless, glistening scales, m. p. 190°. When the product obtained on saponification is diazotised, it forms 3 : 4-*dimethoxyxanthone*, $C_{15}H_{12}O_4$, which separates from a mixture of benzene and light petroleum in yellow needles, m. p. 155°, and gives a green fluorescence with concentrated sulphuric acid.

p-*Toluenesulphone-2-aminophenyl α-methoxynaphthyl ketone*,

$C_{25}H_{21}O_4NS$,

obtained by the condensation of *p*-toluenesulphoneanthranilic chloride with α-naphthyl methyl ether, separates from alcohol in colourless leaflets, m. p. 192°. When saponified, it forms 2-*aminophenyl α-methoxynaphthyl ketone*, $C_{18}H_{15}O_2N$, which separates from dilute alcohol in yellow, glistening crystals, m. p. 147°, and on diazotisation forms *α-methoxynaphthafluorenone*, $C_{18}H_{12}O_2$, which crystallises from alcohol in orange-red needles, m. p. 183°, and forms a yellowish-green solution with concentrated sulphuric acid. 2-*Hydroxyphenyl α-methoxynaphthyl ketone*, $C_{18}H_{14}O_3$, crystallises from dilute alcohol in yellow leaflets, m. p. 124°.

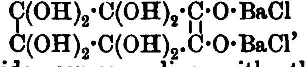
p-*Toluenesulphone-2-aminophenyl β-methoxynaphthyl ketone*,

$C_{25}H_{21}O_4NS$,

obtained from β-naphthyl methyl ether, separates from alcohol in glistening crystals, m. p. 181°. When heated with concentrated sulphuric acid in the usual manner it undergoes sulphonation as well as saponification, forming 2-*aminophenyl β-methoxynaphthyl-ketone-sulphonic acid*, $C_{18}H_{15}O_5NS$, which separates in yellow crystals. When diazotised, the latter yields a product the solution of which in sulphuric acid is yellow and exhibits a green fluorescence, and is accordingly a xanthone derivative.

1 : 2-*Phenonaphthacridone*, $C_{17}H_{11}ON$, obtained by heating *p*-toluenesulphone-2-aminophenyl β-methoxynaphthyl ketone with hydrochloric acid at 150—180°, separates from pyridine in brownish-yellow needles, m. p. 383°. Its alcoholic solution exhibits a blue fluorescence; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence.

A. McK.

Triquinoyl. FRANZ HENLE (*Annalen*, 1906, **350**, 330—343. Compare Nietzki and Benckiser, Abstr., 1885, 779, 1127; Nietzki and Schmidt, Abstr., 1888, 690, 943).—Triquinoyl is readily soluble in moderately concentrated solutions of sodium, potassium, ammonium, calcium, barium, or magnesium chloride, potassium iodide, or potassium or sodium nitrate at the ordinary temperature, but is only sparingly so in alkali sulphates, and is insoluble in mercuric chloride solutions. It may be purified by solution in hot aqueous sodium chloride, from which on cooling more than 60% separates, m. p. 98°, or after recrystallisation from dilute nitric acid, m. p. 100° (decomp.). These solutions of triquinoyl decompose slowly at the laboratory temperature, more quickly when heated, evolving carbon dioxide and forming rhodizonic acid. The solution in aqueous barium chloride yields a red *barium* salt,  $\begin{matrix}C(OH)_2\cdot C(OH)_2\cdot C\cdot O\cdot BaCl\\ \vert \qquad\qquad\qquad\quad \Vert \\ C(OH)_2\cdot C(OH)_2\cdot C\cdot O\cdot BaCl\end{matrix}$, together with a volume of carbon dioxide corresponding with the equation $7C_6O_6 + 6H_2O = 6C_6H_2O_6 + 6CO_2$; the red salt is only slowly decomposed by boiling water, forming barium rhodizonate and chloride. The formation of this salt serves for the characterisation of triquinoyl.

The action of baryta on triquinoyl in aqueous solution leads to the formation, according to the conditions, of four salts: a *red* salt, $C_6O_6,3H_2O,3baOH$, and three *white* salts: $C_6O_6,4H_2O,5baOH$; $C_6O_6,4H_2O,4baOH$, and $C_6O_6,3H_2O,4baOH$ respectively. The results obtained on titration of triquinoyl with baryta agree with the compositions of the salts $C_6O_6,4H_2O,5baOH$ and $C_6O_6,4H_2O,4baOH$. When treated with hydrochloric or sulphuric acid, the red salt yields carbon dioxide and rhodizonic acid, whilst the white salts form carbon dioxide and a syrup which reduces silver nitrate and Fehling's solutions in the cold.

Triquinoyl is soluble in acetic anhydride in presence of traces of concentrated sulphuric acid, in ether when shaken with phosphorus pentoxide, or in methyl alcohol in presence of traces of hydrogen chloride. On evaporation in a vacuum at 20°, the methyl alcoholic solution yields crystalline triquinoyl, but if first shaken with anhydrous sodium sulphate, a yellow syrup, which readily decomposes, evolving carbon dioxide, and forms crystalline triquinoyl only on addition of water. The action of sodium acetate on the methyl alcoholic solution leads to the formation of sodium rhodizonate; the action of anhydrous ammonia on the ethereal or methyl alcoholic solution leads to that of a blackish-red *substance*, which is converted by water into ammonium rhodizonate.

Anhydrous triquinoyl, C_6O_6, which must be present in the ethereal and methyl alcoholic solutions, is formed also together with silver bromide when silver rhodizonate is treated with bromine in ethereal solution. G. Y.

Buchu-camphor. IWAN L. KONDAKOFF (*Chem. Zeit.*, 1906, **30**, 1090—1091 and 1100—1101).—Polemical. The author maintains that the results published by Semmler and McKenzie (Abstr., 1906, i, 373) are in the main a repetition of his own (Abstr., 1905, i, 798).

The paper contains a historical summary of the work which has been done on this subject. P. H.

Components of Ethereal Oils. I. Resolution of the Bicyclic Triocean System in Sabinene and Tanacetone. II. A New Series of Terpenes (*cyclo*Pentadienes). FRIEDRICH W. SEMMLER (*Ber.*, 1906, **39**, 4414—4428).—From tanacetone both *cyclo*hexane and *cyclo*pentane derivatives can be obtained, whereas in the case of bicyclic hydrocarbons only the conversion into terpinenes or limonenes, both *cyclo*hexane derivatives, is known. It has hitherto not been possible to break the three-membered ring in the bicyclic triocean system of sabinene and obtain a *cyclo*pentane derivative.

By the action of formic acid on sabinene, a product is obtained which is separated into two fractions on distillation. The one, a *formate*, $C_{11}H_{18}O_2$, b. p. 102—106°/10 mm., α_D +14°15′ (100 mm.), n_D 1·4745, D^{20} 0·975, yields on hydrolysis an *alcohol*, $C_{10}H_{18}O$, b. p. 93—96°/11 mm., n_D 1·48033, D^{20} 0·926, which forms a dihydrochloride, m. p. 51—52°, identical with that formed on acting on sabinene with acetic acid and hydrogen chloride, and probably identical with terpinene dihydrochloride. On oxidation with permanganate, the alcohol forms a glycerol, $C_{10}H_{18}O_3$, b. p. 175—177°/10 mm., which crystallises from chloroform and is perhaps identical with the glycerol obtained by Biltz (Abstr., 1899, i, 535) from origanol (*p*-methyl*iso*propyl*cyclo*hexenol). The formate on distillation with quinoline forms a terpene, $C_{10}H_{16}$, b. p. 174—177°, n_D 1·479, D^{20} 0·839. The alcohol, $C_{10}H_{18}O$, is thus a mixture of dimethyl*iso*propyl*cyclo*pentenol and origanol.

The second product of the action of formic acid on sabinene is a terpene, $C_{10}H_{16}$, b. p. 50—54°/10 mm., 169—173°/760 mm., n_D 1·47, D^{20} 0·829—0·831, α_D +13—14° (10 mm. tube), M.R. 45·71, which constants point to its being a *cyclo*pentadiene. E. F. A.

Sandarac. ALEXANDER TSCHIRCH and MAX WOLFF (*Arch. Pharm.*, 1906, **244**, 684—712. Compare Tschirch and Balzer, Abstr., 1896, i, 493; Henry, Trans., 1901, 1144).—The resin examined had D 1·071, acid number 141, and saponification number 166. Some of it was submitted to dry distillation: among the products, acetic acid was detected, but not butyric acid or acetic acid; attempts to isolate retene were unsuccessful.

From an ethereal solution of the resin, 1% aqueous ammonium carbonate extracted amorphous *sandaracic acid*, $C_{22}H_{34}O_8$, in 2·3% yield; m. p. 186—188° (decomp.), has acid number 163 (corresponding with monobasicity), and saponification number 175, and does not contain methoxyl.

With 1% aqueous sodium carbonate, acids were then extracted in 87% yield. The bulk of these consisted of an amorphous acid of which the lead salt is insoluble in alcohol, *sandaracinolic acid*, $C_{24}H_{36}O_3$; this decomposes at 265—275°, has acid number 160 (corresponding with monabasicity), and saponification number 169, does not contain methoxyl, and forms with acetic anhydride a product that yields acetic acid when hydrolysed. Mixed with this acid is a small quantity of another, *sandaracopimaric acid*, $C_{20}H_{30}O_2$; this is crystalline, has m. p. 170°, acid number 187 (corresponding with monobasicity), saponification number 194, and iodine number 140 (addition of 3I requires 126); it forms an amorphous *silver* salt containing Ag 26·7%; it does not contain methoxyl or form an acetyl derivative. From the later portions of sodium carbonate solution used in the extraction, when they were allowed to remain, a crystalline *sodium* salt separated in yield equal to 0·7% of the resin; this melted at 83—85°, dissolved in benzene as well as in water, and contained Na 7·7%; the corresponding *silver* salt contained Ag 22·4%; the *acid* decomposed at 146—148°, contained C 71—76%, H 9·4%, and seemed to undergo slowly a transformation of which the *bitter principle*, which also occurs in the resin itself, is a product.

From the remaining ethereal solution, aqueous potassium hydroxide, even of 50% strength, did not extract anything. The ether was distilled off, and the residue steam-distilled, when an *essential oil*, of b. p. 152—159°, distilled over in 1·3% yield, while amorphous *sandaracoresen*, $C_{22}H_{36}O_2$, of m. p. 57°, remained in 3·3% yield; the resin appears to undergo spontaneously a slow transformation of which acid and essential oil are products.

The acids obtained are optically inactive, even before the treatment with alkali.
C. F. B.

Molecular Weight of Elaterin. ARMAND BERG (*Compt. rend.*, 1906, **143**, 1161—1163. Compare Abstr., 1898, ii, 447; 1906, i, 596).—Chiefly polemical against Pollak (Abstr., 1906, i, 973). Further evidence in favour of the formula $C_{28}H_{38}O_7$ for elaterin is afforded by the results of the analyses of the *sodium*, *cadmium*, and *copper* salts of elateric acid.
M. A. W.

Reduction of the Furan Nucleus. MAURICE PADOA and U. PONTI (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 610—615. Compare Abstr., 1906, i, 530).—When mixed with hydrogen and passed over reduced nickel heated at about 190°, furfuraldehyde vapour yields mainly furfuryl alcohol, together with small proportions of more highly hydrogenated compounds. To obtain larger quantities of the latter, furfuryl alcohol itself was reduced in the above manner, the products then obtained being 2-methylfuran, 2-methyltetrahydrofuran, *a*-methyl-*n*-butyl alcohol, and methyl propyl ketone.

When passed over reduced nickel heated at about 270°, furfuraldehyde vapour is decomposed into carbonic oxide and furan.
T. H. P.

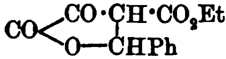
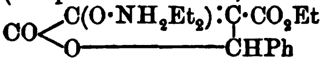
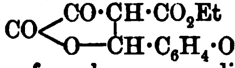
Ethyl Pyromucylacetate [Furfuroylacetate]. HENRY A. TORREY and JOAQUIN E. ZANETTI (*Amer. Chem. J.*, 1906, **36**, 539—543).—Ethyl furfuroylacetate, prepared by Sandelin's method (Abstr., 1900, i, 305), is a pale yellow, heavy oil, b. p. 143—145°/10 mm. Its *oxime*, $C_4OH_3\cdot C(NOH)\cdot CH_2\cdot CO_2Et$, crystallises from aqueous alcohol in long, silky needles, m. p. 131—132°. Its *semicarbazone*,

$$C_4OH_3\cdot C(N_2H\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2Et,$$

crystallises from alcohol in flat, rhombic plates, m. p. 142—144°.

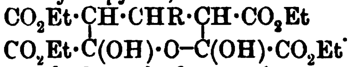
Acetyl-1-*phenyl*-3-*furylpyrazolone*, $C_{13}H_9O_2N_2Ac$, crystallises from light petroleum in flat, faintly yellow prisms, m. p. 69—72°. *Benzoyl*-1-*phenyl*-3-*furylpyrazolone*, $C_{13}H_9O_2N_2Bz$, crystallises from aqueous alcohol in white needles, m. p. 113—114°, and dissolves in alcohol or ether. *Nitroso*-1-*phenyl*-3-*furylpyrazolone*, $C_{13}H_9O_2N_2\cdot NO$, separates from aqueous alcohol as a bright red, amorphous, hygroscopic precipitate, softens at about 170°, and decomposes at 183—184°. T. H. P.

The Pyran Series. II. Condensation of Ethyl Oxalacetate with Cyclic Aldehydes. H. GAULT (*Bull. Soc. chim.*, 1906, [iii], **35**, 1264—1275. Compare Abstr., 1904, i, 762; 1906, i, 300).—This series of ketoarylparaconic esters has been obtained by condensing ethyl oxalacetate with cyclic aldehydes: (1) by Wislicenus' method (Abstr., 1893, i, 146 and 714), condensation by means of hydrogen chloride, or (2) by condensation in presence of diethylamine, the diethylamine derivative being first obtained in the latter case. All the esters give red colorations with ferric chloride and are soluble in aqueous solutions of alkali carbonates, from which they are reprecipitated unchanged on the addition of acids.

Ethyl ketophenylparaconate,  $\mathrm{CO}\Big<\begin{array}{l}\mathrm{CO\cdot CH\cdot CO_2Et}\\ \mathrm{O{-}{-}CHPh}\end{array}$, m. p. 104—105° (compare Wislicenus, *loc. cit.*), furnishes a *diethylamine* derivative,  $\mathrm{CO}\Big<\begin{array}{l}\mathrm{C(O\cdot NH_2Et_2):C\cdot CO_2Et}\\ \mathrm{O{-}{-}{-}{-}{-}{-}{-}{-}CHPh}\end{array}$, which is formed when benzaldehyde is condensed with ethyl oxalacetate in presence of diethylamine, and separates from alcohol in colourless crystals, m. p. about 160° (decomp.). *Ethyl ketoanisylparaconate*,  $\mathrm{CO}\Big<\begin{array}{l}\mathrm{CO\cdot CH\cdot CO_2Et}\\ \mathrm{O{-}{-}CH\cdot C_6H_4\cdot OMe}\end{array}$, similarly obtained from anisaldehyde, separates from benzene or dilute alcohol in crystals, m. p. 96°. The *diethylamine* derivative forms colourless crystals, m. p. about 160° (decomp.). *Ethyl keto*-o-*nitrophenylparaconate*, similarly prepared from *o*-nitrobenzaldehyde, separates from alcohol in colourless crystals, m. p. 115°. The *diethylamine* derivative forms small, faintly yellow crystals, m. p. about 165° (decomp.). *Ethyl keto*-m-*nitrophenylparaconate* separates from benzene or alcohol in crystals, m. p. 96°, and yields a *diethylamine* derivative which is faintly yellow, m. p. about 165° (decomp.). *Ethyl keto*-p-*hydroxyphenylparaconate*, m. p. 184°, crystallises from alcohol; the *diethylamine* derivative separates from dilute alcohol in crystals and melts and decomposes about 165°.

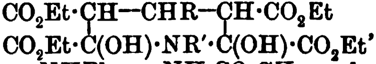
When ethyl oxalacetate is condensed with salicylaldehyde in presence of hydrogen chloride there is formed *ethyl salicylideneoxalacetate hydrochloride*, $CO_2Et\cdot CO\cdot C(CO_2Et):CH\cdot C_6H_4\cdot OH,HCl$, m. p. 98°, which crystallises from light petroleum; it readily loses HCl when warmed alone or when treated in the cold with potassium carbonate or potassium hydrogen carbonate, yielding the free *ester* which is obtained directly when the condensation is effected in presence of piperidine or diethylamine. The ester separates from dilute alcohol in crystals, m. p. 91°; its alcoholic solution is not coloured by ferric chloride. T. A. H.

The Pyran Series. III. Condensation of Ethyl Oxalacetate with Aliphatic Aldehydes. H. Gault (*Bull. Soc. chim.*, 1907, [iv], 1, 21—32).—Aliphatic aldehydes condense with ethyl oxalacetate in presence of piperidine to form the corresponding ethyl alkylidenebisoxalacetates, $CHR[CH(CO_2Et)\cdot CO\cdot CO_2Et]_2$. These are crystalline solids and combine with a molecule of water to form hydrates which are derivatives of tetrahydropyran, thus:



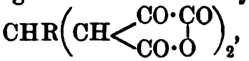
$$\begin{array}{l} CO_2Et\cdot CH\cdot CHR\cdot CH\cdot CO_2Et \\ CO_2Et\cdot C(OH)\cdot O - C(OH)\cdot CO_2Et \end{array}$$

Alcoholic solutions of these hydrates give a red coloration with ferric chloride on warming, and furnish monophenylhydrazones and monosemicarbazones of the following constitution:



$$\begin{array}{l} CO_2Et\cdot CH - CHR - CH\cdot CO_2Et \\ CO_2Et\cdot C(OH)\cdot NR'\cdot C(OH)\cdot CO_2Et' \end{array}$$

where R^1 may be $-NHPh$ or $NH\cdot CO\cdot CH_2$, and are hydrolysed by dilute acids, forming αε-diketonic acids, and by cold sulphuric acid, forming the corresponding bisoxalacetic dianhydrides,



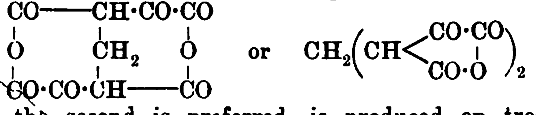
$$CHR\left(CH{<}\begin{array}{l}CO\cdot CO \\ CO\cdot O\end{array}\right)_2,$$

which in contact with water are transformed into the corresponding unstable di-β-ketonic acids; these readily lose carbon dioxide and form αε-diketopimelic acids (compare Abstr., 1904, i, 762; 1906, i, 300).

Ethyl methylenebisoxalacetate, obtained from formaldehyde by the general method (*loc. cit.*), furnishes a *hydrate*, m. p. about 112°, which crystallises from dilute alcohol and is slightly soluble in cold, but readily so in hot alcohol. The *hydrosulphide*, obtained by treating a solution of the ether in alcohol with hydrogen sulphide, crystallises from ether on addition of light petroleum in small needles, m. p. 118°, and is regarded as having a constitution analogous to that of the hydrate. Both the hydrate and hydrosulphide regenerate ethyl methylenebisoxalacetate when heated at 110°. The *monophenylhydrazone*, m. p. 143°, obtained by the action of phenylhydrazine on the hydrate dissolved in alcohol, crystallises from dilute alcohol and is coloured red by ferric chloride on warming. The anhydrous ether furnishes a *diphenylhydrazone*, m. p. 211°, which separates from acetone in woolly crystals. The *monosemicarbazone* yielded by the hydrated ether crystallises from boiling water; m. p. 167° (decomp.).

Methylenebisoxalacetotetra-amide, m. p. about 170° (decomp.), is produced when either the ether or its hydrate, dissolved in alcohol, is treated with dry ammonia; it is coloured red by ferric chloride. *Methylenebisoxalacetotetrabenzylamidedibenzylimide*, obtained by condensing benzylamine with the anhydrous ether, crystallises from boiling acetone and has m. p. 216—217°.

Methylenebisoxalacetic dianhydride, represented by the formula



$$\begin{array}{l} CO\text{——}CH\cdot CO\cdot CO \\ O \qquad CH_2 \qquad O \\ CO\cdot CO\cdot CH\text{——}CO \end{array} \quad \text{or} \quad CH_2\left(CH{<}\begin{array}{l}CO\cdot CO \\ CO\cdot O\end{array}\right)_2,$$

of which the second is preferred, is produced on treating ethyl methylenebisoxalacetate with sulphuric acid. It is very unstable, and in contact with a minute quantity of water at 0° forms a crystalline *monohydrate,* which when allowed to dry in the air loses carbon dioxide, but when dried over sulphuric acid under reduced pressure regenerates the dianhydride. The latter with excess of water dissolves and passes into the unstable diketonic tetracarboxylic acid, which decomposes rapidly, giving rise to diketopimelic acid (Abstr., 1905, i, 763). The dianhydride on treatment with aniline yields a dianilide, which also decomposes readily, forming the dianilide of diketopimelic acid. The latter acid is also produced directly by boiling the dianhydride with dilute acids. T. A. H.

Constituents of the Leaves of Carpinus Betulus. Ellagic Acid and Tannic Acids. KARL ALPERS (*Arch. Pharm.*, 1906, **244**, 575—601).—The author sums up the results of his investigation as follows. The leaves of the hornbeam (*Carpinus Betulus, L.*) contain a glucoside from which ellagic acid is eliminated very readily, even in the extraction of the leaves with 40% alcohol. Neither glucosides nor aldehyde could be detected. Methyl alcohol and acetone, as well as ethyl alcohol, dissolve ellagic acid to an appreciable, although slight, extent; in all other of the usual solvents, ellagic acid is practically insoluble. Ellagic acid chars at 450—480° without first melting. The shape of its crystals varies; under the microscope it appears to consist of short, rhombic prisms and long, prismatic needles. The constitution of ellagic acid probably is best expressed by Graebe's formula (Abstr., 1903, i, 262); the water that air-dried ellagic acid loses at 100° possibly is anhydride water and not water of crystallisation; in that case the air-dried acid might be regarded as hexahydroxydiphenyldicarboxylic acid, and the acid after drying at 100° as the dilactone of this as represented by Graebe's formula.

The tannin of hornbeam leaves has much similarity with ellagitannic acid (Löwe, *Zeit. anal. Chem.*, 1875, **14**, 35); it yields gallic acid when hydrolysed. No glucosidic character could be detected in the tannin; in this respect it differs from the tannin of myrobalans, of algarobilla, and of divi-divi pods. C. F. B.

Behaviour of Alkaloid Salts and of other Organic Substances with Regard to Solvents. Reducing Action of Alkaloids. A. SIMMER (*Arch. Pharm.*, 1906, **244**, 672—684).—Aqueous solutions of salt of the alkaloids, containing 0·4% of the base, were percolated with solvents; so also were solutions containing the same percentage of alkaloid with excess of acid. The stronger the base the less of it passed into the organic solvent: chloroform dissolved out hardly appreciable amounts of nicotine and atropine; more veratrine, strychnine, brucine, codeine, cocaine, and morphine; and still more narcotine, papaverine, colchichine, caffeine, and antipyrine. In the presence of excess of acid, the amount of the stronger alkaloids extracted was much diminished; if the salt itself is soluble in chloroform, the amount of it extracted increases up to a certain point with the excess of free acid, if this be hydrochloric, hydrobromic, or nitric; if it be sulphuric, phosphoric, citric, or tartaric, of which the alkaloid salts are insoluble in chloroform, none of the alkaloid is dissolved out, provided in the case of the last two acids that the excess of them is considerable.

Similar experiments were made with the sodium derivatives of picrotoxin, santonin, coussein, cantharidin, and salicylic acid, with and without excess of sodium hydroxide. In the absence of the latter all but cantharidin passed into the chloroform in appreciable quantity; in the presence of sodium hydroxide only coussein and picrotoxin, and of these but traces.

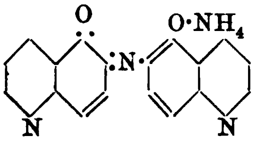
Experiments were also made with benzene and ether, in both of which alkaloids and alkaloid salts are less soluble than in chloroform, with carbon tetrachloride, and in the case of morphine, with amyl and *iso*butyl alcohols.

Many of the numerical results are tabulated.

When an alkaloid mixed with chloroform and water was percolated with chloroform for eight hours, in the cases of brucine, veratrine, strychnine, atropine, and cocaine, the chloroform was found to contain chloride equivalent to an amount of the alkaloid decreasing in the order named from 1·7% to 0·2% of the whole; in other cases there was no such action. Formation of formic acid could not be detected. The action of certain alkaloids and their salts in *N*/200 alcoholic or aqueous solution on various oxidising agents was studied, namely, silver nitrate, gold chloride, mercuric chloride, ferric salts, acid permanganate solution, &c. Morphine is particularly active as a reducing agent, atropine and cocaine were the only ones that did not reduce permanganate appreciably. The salts did not reduce silver nitrate or mercuric chloride; with gold chloride this difference between the alkaloids and their salts was not manifested to the same extent. C. F. B.

The Thalleioquinine Reaction. Hermann Fühner (*Arch. Pharm.*, 1906, **244**, 602—622).—An attempt to throw light on the nature of the thalleioquinine reaction. As the reaction is given not only by quinine but also by cupreine, it would seem that the reaction must be attributed to the *p*-hydroxyquinoline group. In the first phase, the action of chlorine water converts this into a dichloroketone, in the second phase this is converted by ammonia into a quinonimine colouring matter. The constitution of the chlorine substitution products obtained from *p*-quinanisole and quinine, where the contained phenol group is methylated, is a matter for further research.

5:5-Dichloro-6-ketoquinoline, $C_9H_5ONCl_2$ (Abstr., 1905, i, 828), yields 5-chloro-6-hydroxyquinoline, C_9H_6ONCl, when it it boiled with dilute alcohol; when it is heated with aniline in alcoholic solution at 50° it yields *5-chloro-6-hydroxy-8-anilinequinoline*, $C_{15}H_{11}ON_2Cl$, m. p. 127—128°, which forms both yellow and dark brown crystals; when a solution of it in dilute alcohol is mixed at once with an excess of ammonia, it yields dark blue, amorphous, colloidal *thalleioquinoline*, $C_{18}H_{14}O_2N_4$, probably having the annexed constitution



, analogous with that of thalleioquinine. It is essential that an excess of ammonia be added at once; when ammonia is added gradually, the precipitate obtained is brown.

The urine of a dog to which quinoline had been administered was found to be coloured green by ammonia after it had been boiled with hydrochloric acid. The presence of 5 : 6-quinolinequinone was detected; and it was found by a special experiment that this substance, like the dichloroketoquinoline, reacts with ammonia to form thalleioquinoline.

C. F. B.

Constitution of Hordenine. EUGÈNE LÉGER (*Compt. rend.*, 1906, **143**, 916—918).—The author has shown already that hordenine has the formula $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2$ (Abstr., 1906, i, 204, 761), and in the present paper it is shown that the hydroxyl group is in the para-position, because when the acetyl derivative of hordenine is oxidised by potassium permanganate, *p*-acetoxybenzoic acid is formed. Hordenine is therefore *p*-hydroxyphenylethyldimethylamine.

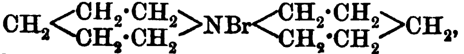
M. A. W.

A Fifth Methylmorphimethine. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, **39**, 4412—4414).—The fifth or *ε-methylmorphimethine* is obtained as a lævorotatory oil by the action of boiling sodium hydroxide on ψ-codeine methiodide; the *hydrochloride* crystallises in large, glistening cubes, m. p. 150° (decomp.), the *methiodide* in needles, m. p. 195—200°, whilst *acetyl-ε-methylmorphimethine methiodide* forms sparingly soluble needles, m. p. 205—210°. E. F. A.

Conversion of Chlorocodide into ψ-Codeine. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1906, **39**, 4409—4411).—By acting on chlorocodide with water at 140—150°, Göhlich (Abstr., 1893, i, 675) showed that codeine was formed. On adding, however, acetic acid to an emulsion of chlorocodide and warm water, the substance obtained is identical with Merck's ψ-codeine (Abstr., 1891, 1121). The *hydriodide*, m. p. 260—265°, crystallises in glistening plates; the *methiodide*, m. p. 270°, also forms large, glistening plates. The *hydriodide* of *acetyl-ψ-codeine* separates in opaque, anhydrous crystals decomposing at 285°. E. F. A.

Cyclic Imines. III. JULIUS VON BRAUN, CARL MÜLLER, and ERICH BESCHKE (*Ber.*, 1906, **39**, 4347—4357. Compare Abstr., 1905, i, 826; this vol., i, 28).—1-Alkylpiperidines are obtained in good yield from αε-dibromopentane (1 mol.) and primary amines (3 mols.) (compare Abstr., 1904, i, 841).

Pentamethylenepiperidinium bromide,



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{NBr}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2},$$

which the author terms *dipiperidinium bromide*, obtained from αε-dibromopentane and piperidine in nearly quantitative yield in chloroform solution, forms a snow-white, crystalline mass. The *platinichloride*, $C_{10}H_{20}NPtCl_6$, darkens at 225°, m. p. 245° (decomp.).

ε-Piperidino-Δ^{α}-pentene (*1-amylenepiperidine*),

$$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH{:}CH_2,$$

b. p. 201—202°, obtained by the action of moist silver oxide on the preceding bromide, is a colourless liquid with a basic odour; the *platinichloride* has m. p. 99—101°; the *picrate*, 93—94°, and the *methiodide*, 159°. By treatment with concentrated hydrobromic acid at 0° it yields 1-δ-*bromoamylpiperidine*, $C_5H_{10}N\cdot C_5H_{10}Br$, the *picrate* of which has m. p. 122°. The free base is very unstable, changing readily into Scholtz and Friemehlt's pentamethylene-2-methylpyrrolidinium bromide (Abstr., 1899, i, 541).

Pentamethylenepiperidinium bromide reacts extremely slowly with concentrated ammonia at 225°, forming a triacid *base*, $C_{20}H_{41}N_3$, b. p. 185—187°/22 mm., of which the *hydrochloride*, the *platinichloride*, m. p. 229° (decomp.), and the *aurichloride*, m. p. 170—171°, are described. C. S.

Action of Grignard's Reagent on certain Indolenines.

Giuseppe Plancher and **C. Ravenna** (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 555—561).—When 2 : 3 : 3-trimethylindolenine or 2 : 3 : 3 : 5-tetramethylindolenine is treated with Grignard's reagent, it is transformed into the corresponding dimolecular polymeride, the compound behaving as if it had the tautomeric methyleneindoline formula $C_6H_4<\genfrac{}{}{0pt}{}{CRR}{NH}>C{:}CH_2$. As the pure indolenines undergo polymerisation of themselves, Grignard's reagent here plays the part of a catalyst.

Under the action of magnesium phenyl bromide or magnesium methyl iodide, 2 : 3 : 3-trimethylindolenine yields the *polymeride* $(C_{11}H_8N)_2$, which separates from alcohol in pale yellow crystals, m. p. 132°, and is reconverted into the unimolecular base if heated above its melting point; with nitrous acid in acetic acid solution it gives the oxime of 2 : 3 : 3-trimethylindolenine; if the polymeride is dissolved in very dilute hydrochloric acid and the solution immediately rendered alkaline, it is reprecipitated in a flocculent condition, but generally the liquid base is attained.

Magnesium methyl iodide also acts on 2 : 3 : 3 : 5-tetramethylindolenine, converting it into the *polymeride* $(C_{12}H_{15}N)_2$, which separates from alcohol or light petroleum in pale yellow crystals, m. p. 111—112°, and is less readily polymerised than the polymeric 2 : 3 : 3-trimethyl derivative.

The interaction of magnesium phenyl bromide and 2-methyl-3 : 3 : diethylindolenine also yields a solid *base*.

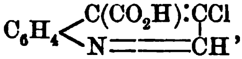
The action of magnesium phenyl bromide on acetophenoneanilide gives a *compound*, $CPh_2Me\cdot NHPh$ (?), m. p. 94—96°. T. H. P.

New Method of Preparation of 1-Methylindole.

Oreste Carrasco and **Maurice Padoa** (*Atti R. Accad. Lincei*, 1906, [v], 15, ii, 729—731. Compare Abstr., 1906, i, 695).—On passing dimethyl-*o*-toluidine, drop by drop, through a tube containing reduced nickel heated at 300—330°, part of the base yields 1-methylindole and part undergoes demethylation, giving rise to methyl-*o*-toluidine, *o*-toluidine, and probably methane. By mixing the dimethyl-*o*-toluidine with hydrogen before passing it over the heated nickel, the yield of 1-methylindole is raised from 6 to 24%; the yield of indole from methyl-*o*-toluidine (*loc. cit.*) is raised in the same way from 6 to 8%.

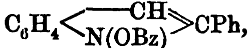
Under the above conditions, ethyl-*o*-toluidine yields a small proportion of a product of an indolic character, probably 2-methylindole.

T. H. P.

Action of Chloroform and Potassium Hydroxide on Scatole [3-Methylindole]. Alexander Ellinger and Claude Flamand (*Ber.*, 1906, **39**, 4388—4390. Compare Abstr., 1906, i, 696).—3-Chloro-4-methylquinoline is formed by the action of chloroform and potassium hydroxide on 3-methylindole in alcoholic solution (Magnanini, Abstr., 1887, 1113). The constitution of the chloromethylquinoline was determined by heating the base with formaldehyde in a closed tube at 100°, and oxidising the resulting methylol compound with nitric acid, D 1·4, 3-*chloroquinoline*-4-*carboxylic acid*,  $C_6H_4<\begin{array}{l}C(CO_2H):CCl\\ N=\!=\!=\!=CH\end{array}$, was obtained, m. p. 262—263° (decomp.). The position of the chlorine atom was established by heating the acid 2—5° above its temperature of decomposition when 3-chloroquinoline was formed. The combined action of chloroform and alkali, therefore, consists in the introduction of the CCl residue between positions 2 and 3 in the indole nucleus. The m. p. of 3-chloroquinoline aurichloride is 183°, not 173° as previously stated (*loc. cit.*).

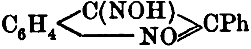
W. R.

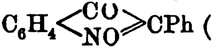
1-Hydroxy-2-phenylindole. Angelo Angeli and Francesco Angelico (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 761—767. Compare Abstr., 1904, i, 526).—1-*Benzoyloxy*-2-*phenylindole*,



$$C_6H_4<\begin{array}{l}—CH—\\ N(OBz)\end{array}>CPh,$$

separates from alcohol in white crystals, m. p. 100°.

3-Nitroso-1-hydroxy-2-phenylindole,  $C_6H_4<\begin{array}{l}C(NOH)\\ —NO\end{array}>CPh$ (*loc. cit.*), yields (1) an *acetyl* derivative, $C_{16}H_{12}O_3N_2$, crystallising from alcohol in yellow needles, m. p. 140°; (2) a *benzoyl* derivative, $C_{21}H_{14}O_3N_2$, crystallising from alcohol in slender, rose-coloured needles, m. p. 163° (decomp.); (3) an *ethyl* derivative, $C_{16}H_{14}O_2N_2$, which separates from light petroleum in orange-coloured crystals, m. p. 96°. Reduction of 3-nitroso-1-hydroxy-2-phenylindole by means of alcohol, hydroxylamine, or hydrazine yields ordinary nitrosophenylindole, whilst zinc, in presence of either acetic acid or ammonium chloride, converts it into 3-amino-2-phenylindole.

Oxidation of 3-nitroso-1-hydroxy-2-phenylindole with chromic acid gives a substance  $C_6H_4<\begin{array}{l}CO\\ NO\end{array}>CPh$ (*loc. cit.*), which crystallises from alcohol in shining, red plates, m. p. 186° and has all the properties of a ketone; reduction of this substance by means of hydroxylamine yields nitrosophenylindole, whilst zinc and acetic acid convert it into a *compound*, $C_{14}H_{11}ON$, which crystallises from benzene in green needles, m. p. 225°, and is probably 3-hydroxy-2-phenylindole.

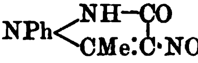
T. H. P.

3-Pyrazolones. II. AUGUST MICHAELIS (*Annalen*, 1906, **350**, 288—329. Compare Abstr., 1905, i, 377).—The 5-pyrazolones yield reddish-yellow *iso*nitroso-derivatives, whilst the action of sodium nitrite on 3-pyrazolones leads to the formation of green nitroso-compounds; on oxidation, both series yield strongly acid nitropyrazolones. On reduction, the *iso*nitroso-5-pyrazolones form unstable aminopyrazolones (Knorr, Abstr., 1887, 678), whereas the 4-amino-3-pyrazolones, obtained from the nitroso-3-pyrazolones, are stable. The 4-amino-3-pyrazolones are highly reactive substances, which in their chemical behaviour closely resemble the primary aromatic amines.

In the present paper a large number of derivatives of 4-amino-1-phenyl-5-methyl-3-pyrazolone and of the corresponding 1-*p*-tolyl-compound are described, as are also a number of 4-alkyl-3-pyrazolones. Whilst in some reactions 5-pyrazolones behave as carbonyl compounds, 3-pyrazolones always react in the hydroxylic form.

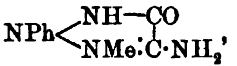
Nitroso- and Amino-derivatives of 3-Pyrazolones.—[With PAUL KOTELMANN.]—4-Nitroso-1-phenyl-5-methyl-3-pyrazolone (Abstr., 1905, i, 244) forms a *hydrochloride*, $C_{10}H_9ON_2\cdot NO,HCl$, which crystallises in slender, yellow needles, m. p. 206°, and is not decomposed when heated with water or alcohol.

4-*Nitro*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,



$\mathrm{NPh}<\begin{matrix}\mathrm{NH-CO}\\ \mathrm{CMe{:}C\cdot NO_2}\end{matrix}$, prepared by the action of concentrated nitric acid on the nitroso-compound in glacial acetic acid solution, forms yellow crystals, m. p. 222°, and dissolves in dilute alkali hydroxides, forming a yellow solution; it is obtained also as a by-product in the preparation of the nitroso-compound.

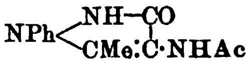
4-*Amino*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,



$\mathrm{NPh}<\begin{matrix}\mathrm{NH-CO}\\ \mathrm{NMe{:}C\cdot NH_2}\end{matrix}$, prepared by reducing the 4-nitroso-compound with zinc and acetic acid, crystallises in glistening, white leaflets, m. p. 182°, becomes red when exposed to air while moist, but is stable when dry, reduces Fehling's solution at the laboratory temperature, or ammoniacal silver nitrate when heated, and gives a red to reddish-brown coloration with bleaching powder solution. The *hydrochloride*, $C_{10}H_{11}ON_3,HCl$, forms white leaflets, m. p. 222°; the *picrate*, $C_{10}H_{11}ON_3,C_6H_2(NO_2)_3\cdot OH$, forms brownish-yellow needles, m. p. 195° (decomp.). The amine forms *condensation products* with the following aldehydes and ketones: $R = C_3N_2HOPhMe$.

With benzaldehyde, $R\cdot N{:}CHPh$: small, yellow crystals, m. p. 248°; anisaldehyde, $R\cdot N{:}CH\cdot C_6H_4\cdot OMe$: slightly blue leaflets, m. p. 245°; cinnamaldehyde, $R\cdot N{:}CH\cdot C_2H_2Ph$: yellow leaflets, m. p. 232°; acetophenone, $CPhMe(NHR)_2$: slender, yellow needles, m. p. 296°, becoming brown; benzophenone, $CPh_2(NHR)_2$: yellow leaflets, m. p. 301°, becoming brown; pyruvic acid, $CO_2H\cdot CMe(NHR)_2$: glistening, white leaflets, m. p. 299°, becoming brown.

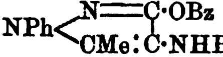
4-*Acetylamino*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,



$\mathrm{NPh}<\begin{matrix}\mathrm{NH-CO}\\ \mathrm{CMe{:}C\cdot NHAc}\end{matrix}$, crystallises in slender, white needles, m. p. 233°. The 4-*formylamino*-

compound, $C_{10}H_9ON_2\cdot NH\cdot COH$, crystallises in white needles, m. p. 197°.

4-*Benzoylamino*-3-*benzoxy*-1-*phenyl*-5-*methylpyrazole*,

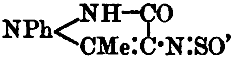


$$NPh<\begin{array}{l}N{=}C\cdot OBz\\ CMe:C\cdot NHBz\end{array},$$

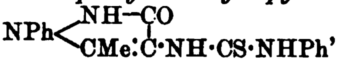
forms colourless crystals, m. p. 176°. 4-*Benzenesulphonylamino*-3-*sulphonoxy*-1-*phenyl*-5-*methylpyrazole*,

$$SO_2Ph\cdot O\cdot C_3N_2PhMe\cdot NH\cdot SO_2Ph,$$

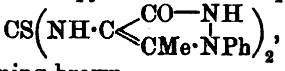
forms large, transparent crystals, m. p. 171°.

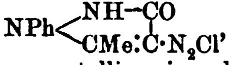
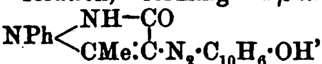
4-*Thionylamino*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,  $NPh<\begin{array}{l}NH-CO\\ CMe:C\cdot N:SO\end{array}$, crystallises in yellow leaflets, m. p. 125°, and is decomposed when heated with aqueous alkali hydroxides.

4-*Phenylthiocarbamido*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,

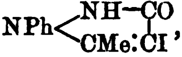


$$NPh<\begin{array}{l}NH-CO\\ CMe:C\cdot NH\cdot CS\cdot NHPh\end{array},$$

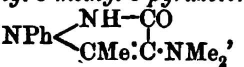
separates from alcohol in small crystals, m. p. 221°, is soluble in aqueous alkali hydroxides, and is decomposed by hot mineral acids, forming phenylthiocarbimide and the 4-aminopyrazolone. *Bis*-1-*phenyl*-5-*methyl*-3-*pyrazolonyl*-4-*thiocarbamide*,  $CS\left(NH\cdot C<\begin{array}{l}CO-NH\\ CMe\cdot NPh\end{array}\right)_2$, forms small, white crystals, m. p. 265°, becoming brown.

The *diazo-chloride*,  $NPh<\begin{array}{l}NH-CO\\ CMe:C\cdot N_2Cl\end{array}$, formed by diazotisation of the 4-aminopyrazolone, crystallises in colourless needles, decomposes at 120°, gradually becomes red on the surface, and gives reactions similar to those of diazobenzene chloride. It couples with β-naphthol in alkaline solution, forming 4-β-*naphtholazo*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,  $NPh<\begin{array}{l}NH-CO\\ CMe:C\cdot N_2\cdot C_{10}H_6\cdot OH\end{array}$, which crystallises in small, yellowish-red leaflets, m. p. 215°. The diazo-chloride forms with resorcinol a dark brownish-red *precipitate*, soluble in an excess of alkali hydroxides, with salicylic acid an orange-red *precipitate*, and with aniline or dimethylaniline a dark red solution yielding a dark red to reddish-brown *precipitate* on addition of sodium acetate.

4-*Azo*-1-*phenyl*-5-*methyl*-3-*pyrazolone*, $N_2(C_3N_2HOPhMe)_2$, formed by the action of the 4-amino-3-pyrazolone on its diazo-chloride, separates as a yellowish-red, crystalline powder, m. p. 160°; the *hydrochloride*, $C_{20}H_{18}O_2N_6,2HCl$, crystallises in red leaflets, m. p. 126°.

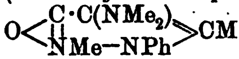
4-*Iodo*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,  $NPh<\begin{array}{l}NH-CO\\ CMe:CI\end{array}$, prepared by boiling the 4-diazo-chloride with aqueous potassium iodide, forms small, yellow crystals, m. p. 207°.

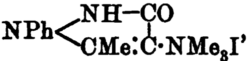
4-*Dimethylamino*-1-*phenyl*-5-*methyl*-3-*pyrazolone*,

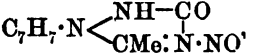


$$NPh<\begin{array}{l}NH-CO\\ CMe:C\cdot NMe_2\end{array},$$

formed with development of heat by the action of methyl iodide, methyl alcohol, and potassium hydroxide on the hydrochloride of the

4-amino-3-pyrazolone, crystallises in matted, slender, white needles, m. p. 188°, is soluble in dilute acids or alkali hydroxides, and when heated on the water-bath with methyl iodide yields *dimethylamino-3-antipyrine* (*4-dimethylamino-*1-*phenyl-*2 : *5-dimethyl-*3-*pyrazolone*; 3-*pyramidone*),  $O<\begin{matrix}C\cdot C(NMe_2)\\ \|\\ NMe-NPh\end{matrix}>CMe$, which is also obtained by the action of methyl sulphate on the 4-amino-3-pyrazolone. It crystallises in slightly yellow needles, m. p. 74°. When heated with methyl iodide under pressure at 100°, it forms the *methiodide*, $C_8N_2OPhMe_2\cdot NMe_3I$, which crystallises in white leaflets, m. p. 126°, and when boiled with silver chloride in aqueous solution yields the *methochloride*; this when heated loses methyl chloride and forms dimethylamino-3-antipyrine.

The *methiodide* of 4-dimethylamino-1-phenyl-5-methyl-3-pyrazolone,  $NPh<\begin{matrix}NH-CO\\ \quad\ \ |\\ CMe:C\cdot NMe_3I\end{matrix}$, formed by boiling the amino-base with methyl iodide and methyl alcohol, crystallises in white leaflets, m. p. 216°.

4-*Nitroso*-1-p-*tolyl*-5-*methyl*-3-*pyrazolone*,  $C_7H_7\cdot N<\begin{matrix}NH-CO\\ \quad\ \ |\\ CMe:N\cdot NO\end{matrix}$, prepared by the action of sodium nitrite on the 3-pyrazolone in glacial acetic acid solution, forms small, green crystals, m. p. 167°; the *hydrochloride*, $C_{11}H_{11}O_2N_3,HCl$, crystallises in slender, yellow needles, m. p. 235°.

4-*Nitro*-1-p-*tolyl*-5-*methyl*-3-*pyrazolone*, $C_{11}H_{11}ON_2\cdot NO_2$, crystallises from alcohol in slender, white needles, m. p. 190°.

4-*Amino*-1-p-*tolyl*-5-*methyl*-3-*pyrazolone*, $C_{11}H_{11}ON_2\cdot NH_2$, m. p. 249°, crystallises from chloroform and has a red lustre; the *hydrochloride*, $C_{11}H_{13}ON_3,HCl$, forms slightly red crystals, m. p. 291°. Condensation products of the amine with the following aldehydes and ketones are described; $R = C_{11}H_{11}ON_2$.

With benzaldehyde, $CHPh:NR$, small, colourless crystals, m. p. 233°; anisaldehyde, $OMe\cdot C_6H_4\cdot CH:NR$, m. p. 235°; cinnamaldehyde, $CHPh:CH\cdot CH:NR$, yellow prisms, m. p. 217°; acetophenone, $CPhMe(NHR)_2$, small, glistening leaflets, m. p. 302°; benzophenone, $CPh_2(NHR)_2$, white leaflets, m. p. 305° (decomp.); pyruvic acid, $CO_2H\cdot CMe(NHR)_2$, white crystals, decomposing at 303°.

4-*Acetylamino*-1-p-*tolyl*-5-*methyl*-3-*pyrazolone*, $C_{11}H_{11}ON_2\cdot NHAc$, crystallises in slender needles, m. p. 244°. The *dibenzoyl* derivative, $OBz\cdot C_{11}H_{10}N_2\cdot NHBz$, forms slender, colourless needles, m. p. 193°. The *dibenzenesulphonyl* derivative forms colourless crystals, m. p. 159°.

4-*Phenylthiocarbamido*-1-p-*tolyl*-5-*methyl*-3-*pyrazolone*,

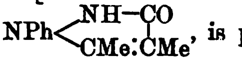
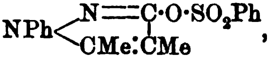
$$C_{11}H_{11}ON_2\cdot NH\cdot CS\cdot NHPh,$$

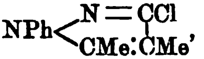
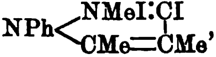
m. p. 220°, crystallises from alcohol.

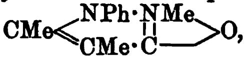
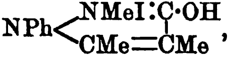
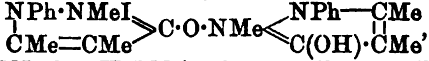
4-*Diazo*-1-p-*tolyl*-5-*methyl*-3-*pyrazolone chloride*, $C_{11}H_{11}ON_2\cdot N_2Cl$, does not decompose when its aqueous solution is evaporated on the water-bath; it couples with β-naphthol forming a dark red, crystalline *azo-dye*, $C_{21}H_{18}O_2N_4$, m. p. 228°. The diazo-chloride also couples with dimethylaniline, salicylic acid, and resorcinol, forming dark red dyes.

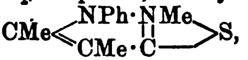
4-*Benzeneazo*-1-*phenyl*- and 4-*Benzeneazo*-1-p-*tolyl*-5-*methylpyrazole*.—[With PAUL KOTELMANN.]—4-Benzeneazo-1-phenyl-5-methylpyrazole cannot be obtained by reduction of 3-chloro-4-benzeneazo-1-phenyl-5-methylpyrazole, but is formed when 4-benzeneazo-1-phenyl-5-methyl-3-pyrazolone is heated with phosphorus pentasulphide at 220—230°; the *hydrochloride*, $C_{16}H_{14}N_4,HCl$, forms dark red needles, m. p. 138°, and gradually decomposes at the laboratory temperature.

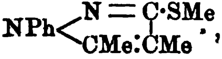
4-*Benzeneazo*-1-p-*tolyl*-5-*methylpyrazole*, $C_{11}H_{11}N_2\cdot N_2Ph$, formed by heating 4-benzeneazo-1-*p*-tolyl-5-methyl-3-pyrazolone with phosphorus pentasulphide at 220—230°, separates from light petroleum in yellowish-red crystals, m. p. 102°; the *hydrochloride*, $C_{17}H_{16}N_4,HCl$, forms yellowish-red needles, m. p. 156°, and readily decomposes.

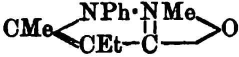
4-*Alkyl*-3-*pyrazolone*.—[With ALEXANDER DREWS.]—1-*Phenyl*-4 : 5-*dimethyl*-3-*pyrazolone*,  $\mathrm{NPh}\Big<\begin{matrix}\mathrm{NH-CO}\\ \mathrm{CMe{:}CMe}\end{matrix}$, is prepared by the action of phosphorus trichloride on a mixture of acetylphenylhydrazine and ethyl methylacetoacetate; it forms small, white needles, m. p. 254°. The *benzenesulphonyl* derivative,  $\mathrm{NPh}\Big<\begin{matrix}\mathrm{N{=\!=}C\cdot O\cdot SO_2Ph}\\ \mathrm{CMe{:}CMe}\end{matrix}$, crystallises in colourless needles, m. p. 97°.

3-*Chloro*-1-*phenyl*-4 : 5-*dimethylpyrazole*,  $\mathrm{NPh}\Big<\begin{matrix}\mathrm{N=CCl}\\ \mathrm{CMe{:}CMe}\end{matrix}$, prepared by the action of phosphorus oxychloride on the pyrazolone at 210° under pressure, is obtained as a white, crystalline mass, m. p. 34°, b. p. 181°/15 mm., is slightly volatile in a current of steam, and when heated with methyl iodide in a sealed tube at 100°, yields 3-*iodo*-1-*phenyl*-4 : 5-*dimethylpyrazolium methiodide*,  $\mathrm{NPh}\Big<\begin{matrix}\mathrm{NMeI{:}CI}\\ \mathrm{CMe{=}CMe}\end{matrix}$, which crystallises in slightly yellow needles, m. p. 217°.

Methyl-3-*antipyrine*,  $\mathrm{CMe}\Big<\begin{matrix}\mathrm{NPh\cdot NMe}\\ \mathrm{CMe\cdot C}\end{matrix}\Big>\mathrm{O}$, prepared by heating the pyrazolone with an excess of methyl iodide in a sealed tube at 100°, crystallises in white leaflets, m. p. 97°, and gives a red coloration with ferric chloride. The *hydriodide*,  $\mathrm{NPh}\Big<\begin{matrix}\mathrm{NMeI{:}C\cdot OH}\\ \mathrm{CMe{=}CMe}\end{matrix}$, forms white needles, m. p. 176°, and on recrystallisation from water yields the crystalline *salt*,  $\begin{matrix}\mathrm{NPh\cdot NMeI}\\ \mathrm{CMe{=}CMe}\end{matrix}\Big>\mathrm{C\cdot O\cdot NMe}\Big<\begin{matrix}\mathrm{NPh-CMe}\\ \mathrm{C(OH)\cdot CMe}\end{matrix}$, m. p. 75°. The *picrate*, $C_{12}H_{15}ON_2\cdot O\cdot C_6H_2(NO_2)_3$, forms yellow needles, m. p. 103°. The *chloride*, $C_{12}H_{14}N_2Cl_2$, m. p. 94°, is very hygroscopic.

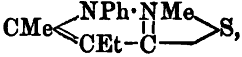
Methyl-3-*thiopyrine*,  $\mathrm{CMe}\Big<\begin{matrix}\mathrm{NPh\cdot NMe}\\ \mathrm{CMe\cdot C}\end{matrix}\Big>\mathrm{S}$, formed by the action of potassium hydrogen sulphide on the iodopyrazole hydriodide in aqueous solution or from the antipyrine chloride by Michaelis and Besson's method (Abstr., 1904, i, 780), separates from water in white crystals, m. p. 103°, and gives a yellow precipitate with sulphurous acid in concentrated solution; the *methiodide*, $C_{13}H_{17}N_2SI$, forms white crystals, m. p. 175°.

3-*Thiomethyl*-1-*phenyl*-4 : 5-*dimethylpyrazole* (*methyl*-ψ-3-*thiopyrine*),  $\mathrm{NPh}\Big<\begin{matrix}\mathrm{N=C\cdot SMe}\\ \mathrm{CMe{:}CMe}\end{matrix}$, prepared by heating the preceding methiodide under reduced pressure, crystallises in long, white needles, m. p. 40°, b. p. 205—208°/20 mm.

1-*Phenyl-5-methyl-4-ethyl-3-pyrazolone*, prepared by the action of phosphorus oxychloride and acetylphenylhydrazine on ethyl ethylacetoacetate, forms white needles, m. p. 172°. The following substances derived from this pyrazolone are described. The *benzenesulphonyl* derivative, $C_{12}H_{13}N_2\cdot O\cdot SO_2Ph$, forms slender needles, m. p. 74°. The 3-*chloropyrazole*, $C_{12}H_{13}N_2Cl$, forms yellow needles, m. p. 92°. The *methiodide* of the 3-iodopyrazole, $C_{13}H_{16}N_2I_2$, m. p. 196°. *Ethyl-3-antipyrine*,  $\mathrm{CMe}<\begin{matrix}\mathrm{NPh\cdot NMe}\\ \mathrm{CEt-C}\end{matrix}>\mathrm{O}$, forms white prisms, m. p. 64°; the *hydriodide*, $C_{13}H_{16}ON_2,HI$, m. p. 175°, when recrystallised from water loses half of its hydrogen iodide and yields the *salt*, $C_{26}H_{33}O_2N_4I$, m. p. 130°, which has a constitution analogous to that of the corresponding methyl-3-antipyrine derivative. The *picrate*,

$$C_{13}H_{16}ON_2,C_6H_3O(NO_2)_3,$$

forms large, yellow crystals, m. p. 83°. *Ethyl-3-thiopyrine*,



$$\mathrm{CMe}<\begin{matrix}\mathrm{NPh\cdot NMe}\\ \mathrm{CEt-C}\end{matrix}>\mathrm{S},$$

crystallises in slender needles, m. p. 120°; the *methiodide*,

$$C_{13}H_{16}N_2S,MeI,$$

forms white crystals, m. p. 108°. *Ethyl-ψ-3-thiopyrine* (3-*thiomethyl-1-phenyl-5-methyl-4-ethylpyrazole*), $C_{12}H_{13}N_2\cdot SMe$, forms a colourless oil, b. p. 160—165°/12 mm.

G. Y.

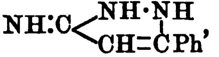
***o*-Carboxylic Azo-compounds and their Transformation into 3-Hydroxyindazyl Derivatives.** PAUL FREUNDLER (*Compt. rend.*, 1906, **143**, 909—911).—The author has shown (Abstr., 1906, i, 544) that benzene-*o*-azobenzoic acid is converted into chloro-3-hydroxy-2-phenylindazole by the action of phosphorus pentachloride or thionyl chloride. The meta- and para-isomerides under similar conditions yield the normal acid chlorides. The benzene-*o*-azochlorobenzoic acid, obtained by oxidising chloro-3-hydroxy-2-phenylindazole, is identical with benzene-2-azo-5-chlorobenzoic acid obtained synthetically as follows. *Methyl-3-chloroacetylanthranilate*, m. p. 127°, obtained by the action of sodium hypochlorite on methyl acetylanthranilate, yields 5-*chloro-anthranilic acid*, m. p. 211—212°,

$$CO_2H\cdot C_6H_3Cl\cdot NH_2[Cl:NH_2:CO_2H=5:2:1],$$

on hydrolysis, which is converted into *p*-chloroaniline when heated at 200°; *methyl-5-chloroanthranilate*, m. p. 69°, b. p. 168—170°/22 mm., condenses with nitrosobenzene to form methyl benzene-2-azo-5-chlorobenzoate, and the corresponding acid is identical with the oxidation product of 5-chloro-3-hydroxy-2-phenylindazole, $C_7N_2H_3PhCl\cdot OH$. Benzene-2-azo-5-chlorobenzoic acid yields a dichloro-3-hydroxy-2-phenylindazole, m. p. 186—187°, by the action of phosphorus pentachloride in which the second chlorine atom probably occupies position 7.

3-*Hydroxy-2-phenylindazole*, $C_7N_2H_4Ph\cdot OH$, m. p. 216—217°, can be prepared from the acetal derivative of benzene-2-azobenzoic acid by the action of dilute sulphuric acid. The lactone of 3-hydroxy-*o*-indazylbenzoic acid (Abstr., 1904, i, 667; Carré, Abstr., 1906, i, 705) can be obtained by reducing *o*-nitrobenzyl alcohol in alkaline medium, or by the action of heat on *o*-hydrazobenzoic acid, or *o*-azobenzoic acid; or by the action of acetic acid on *o*-azoxybenzaldehyde (Bamberger, *private communication*). M. A. W.

Condensation of Hydrazines with Acetylenic Nitriles. General Method of Synthesising Pyrazolonimines [5-Iminopyrazolines]. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1906, **143**, 1239—1242. Compare Abstr., 1906, i, 702—956).—Phenylpropiolonitrile condenses readily with hydrazine hydrate in alcoholic solution to form 5-imino-3-phenylpyrazoline,

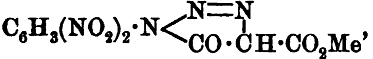


$$\mathrm{NH{:}C}<\begin{matrix}\mathrm{NH\cdot NH}\\ \mathrm{CH{=}CPh}\end{matrix},$$

identical with the compound obtained by Seidel (Abstr., 1899, i, 138) by the action of hydrazine hydrate on cyanoacetophenone; it is probable that the hydrazone $NH_2\cdot N{:}CPh\cdot CH_2\cdot CN$ or $NH_2\cdot NH\cdot CPh\cdot CH\cdot CN$ is first formed and subsequently converted into the isomeride iminopyrazoline, and this explanation of the reaction is supported by the fact that *as*-diphenylhydrazine condenses with phenylpropiolonitrile to form the diphenylhydrazone $NPh_2\cdot NH\cdot CPh{:}CH\cdot CN$, identical with the hydrazone prepared by Seidel (*loc. cit.*) by the action of cyanoacetophenone on diphenylhydrazine.

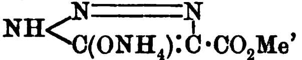
The following iminopyrazolines were prepared. 5-*Imino*-3-*amylpyrazoline*, m. p. 41°, b. p. 205—208°/18 mm. (corr.), and the *picrate*, m. p. 142—144°. 5-*Imino*-1-*phenyl*-3-*amylpyrazoline*, b. p. 231—233°/18 mm. (corr.), D_4^{20} 1·047. 5-*Imino*-3-*hexylpyrazoline*, m. p. 32°, b. p. 214—217°/18 mm. (corr.). 5-*Imino*-3-*phenylpyrazoline*, m. p. 125—126°; the *hydrochloride*, m. p. 78—80°; the *platinichloride*, m. p. 225° (decomp.); the *picrate*, m. p. 202—203° (corr.). 5-Imino-1:3-diphenylpyrazoline, m. p. 127—129° (compare Seidel, Abstr., 1899, i, 138); the hydrochloride is dissociated by excess of water and the *platinichloride* decomposes at 153—155°. M. A. W.

5-Hydroxy-1:2:3-triazole. OTTO DIMROTH and HANS AICKELIN (*Ber.*, 1906, **39**, 4390—4392. Compare Curtius and Thompson, this vol., i, 95).—*Methyl* 1-o-p-*dinitrophenyl*-5-*triazolone*-4-*carboxylate*,



$$C_6H_3(NO_2)_2\cdot N<\begin{matrix}N{=}N\\ CO\cdot CH\cdot CO_2Me\end{matrix},$$

prepared by the nitration of the ester at −5° with fuming nitric acid, crystallises from glacial acetic acid in white needles, m. p. 195°, and is explosive. When this compound is heated with a methyl alcoholic solution of ammonia at 100° for ten hours in a sealed tube, 2:4-dinitroaniline and the *ammonium* salt of *methyl* 5-*hydroxytriazole*-4-*carboxylate*,

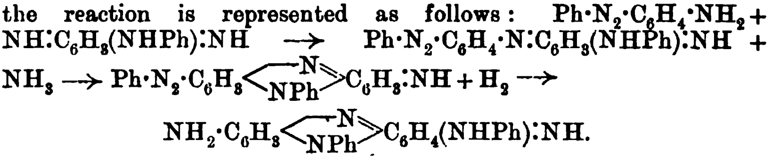


$$NH<\begin{matrix}N{=\!=\!=}N\\ C(ONH_4){:}C\cdot CO_2Me\end{matrix},$$

are formed. The *barium* salt, $(C_4H_4O_3N_3)_2Ba,5H_2O$, crystallises in long, colourless needles. The *ester* crystallises in colourless aggregates and is easily soluble in water, the solution giving with ferric chloride an intense brownish-red coloration, indicating an enolic constitution. By hydrolysing with barium hydroxide and acidifying, a solution of 5-hydroxytriazole-4-carboxylic acid is obtained, and its alkaline solution with a diazotoluene salt yields 4-tolueneazo-5-hydroxytriazole (Curtius and Thompson, *ibid.*). W. R.

Formation of *s*-Safranines. PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1906, [iii], 35, 1278—1282. Compare Abstr., 1906, i, 51, 989).—The method employed is essentially that used by Fischer and Hepp (Abstr., 1903, i, 134), which consists in condensing *p*-aminoazo-compounds under the influence of heat.

When a mixture of *p*-aminoazobenzene and its hydrochloride is heated in phenol at 140—150°, *s*-*anilinophenosafranine* is produced; it is a black, microcrystalline powder with a bronze sheen. It cannot be obtained by condensing aniline with *s*-phenosafranine. It dyes mordanted cotton and silk in bluish-violet shades. The mechanism of the reaction is represented as follows:



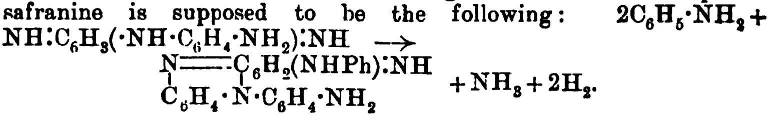
$$\mathrm{Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}NH_2 + NH{:}C_6H_3(NHPh){:}NH \longrightarrow Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}N{:}C_6H_3(NHPh){:}NH + NH_3 \longrightarrow Ph{\cdot}N_2{\cdot}C_6H_3 < \begin{array}{c} N \\ NPh \end{array} > C_6H_3{:}NH + H_2 \longrightarrow}$$

$$\mathrm{NH_2{\cdot}C_6H_3 < \begin{array}{c} N \\ NPh \end{array} > C_6H_4(NHPh){:}NH.}$$

This reaction is possible because in *p*-aminoazobenzene there is, relatively to the amino-group, an *ortho*-position free, which permits the introduction of the aniline residue. This is not the case when *p*-aminoazotoluene is used as a starting point, and consequently when this substance is condensed in the manner just described the product obtained is *s*-*tolusafranine*, which after purification forms reddish-brown crystals with a metallic sheen. Along with the tolusafranine there is produced a violet colouring matter, which after prolonged heating is converted into a red dye and a reddish-yellow substance which appears to be *o*-azotoluene.

p-Aminoazobenzene condenses with benzeneazo-α-naphthylamine, in the manner described, to form *naphthaphenosafranine*, which can be purified by recrystallisation from warm water. Its hydrochloride forms slender, brown needles with a bronze sheen. It dyes mordanted silk and cotton a fine red with shades more bluish than those given by the pheno- and tolu-safranines. T. A. H.

Formation of *as*-Safranines. PHILIPPE BARBIER and PAUL SISLEY (*Bull. Soc. chim.*, 1906, [iii], 35, 1282—1285. Compare Abstr., 1906, i, 51, 989, and preceding abstract).—When a mixture of *p*-diaminoazobenzene hydrochloride and aniline hydrochloride in alcohol is heated in an autoclave at 160—170°, two products are formed, the one having the reactions and properties of *as*-phenosafranine and the other, which is a dark, microcrystalline powder with a metallic sheen, is *as*-*anilinophenosafranine*, $C_{24}H_{19}N_5$. It gives fine, bluish-violet shades on silk and cotton mordanted with tannin and tartar emetic. The mechanism of the reaction which gives rise to *as*-anilinophenosafranine is supposed to be the following:



$$\mathrm{2C_6H_5{\cdot}NH_2 + NH{:}C_6H_3({\cdot}NH{\cdot}C_6H_4{\cdot}NH_2){:}NH \longrightarrow \begin{array}{l} N{=\!=\!=}C_6H_2(NHPh){:}NH \\ C_6H_4{\cdot}N{\cdot}C_6H_4{\cdot}NH_2 \end{array} + NH_3 + 2H_2.}$$

p-*Diaminoazotoluene*, obtained by careful reduction of *p*-nitro-*o*-toluidine, when condensed with *o*-toluidine, as just described, furnishes as-*tolusafranine*, $C_{21}H_{20}N_4$, which is crystalline, has a metallic sheen, and gives superb rose-red shades on silk or cotton, the tones being always more bluish than those of the corresponding phenosafranine. The *platinichloride* is a crystalline powder with a metallic lustre.

T. A. H.

Action of Alkali Hydroxides on *s*-Tribromodiazobenzene.

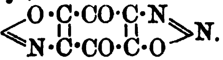
Eugen Bamberger and **E. Kraus** (*Ber.*, 1906, **39**, 4248—4252. Compare Orton, Trans., 1903, **83**, 796; 1905, **87**, 99; Hantzsch, Abstr., 1903, i, 665).—3 : 5-*Dibromo-2-aminophenol*, $OH{\cdot}C_6H_2Br_2{\cdot}NH_2$, is prepared by the action of aqueous sodium hydroxide on diazotised 2 : 4 : 6-tribromoaniline and reduction of the resulting quinonediazide with stannous chloride and glacial acetic acid in hydrochloric acid solution, or by hydrolysis of dibromo-*o*-phenetidine by means of aluminium chloride; it crystallises in long, glistening, colourless, broad needles, m. p. 145°, is readily soluble in aqueous alkali hydroxides, and forms a *hydrochloride* which crystallises in glistening needles, is sparingly soluble in water or dilute hydrochloric acid, and is decomposed by much boiling water. The base gives with alcoholic ferric chloride a violet coloration rapidly becoming brown, and deposits a flocculent precipitate; with calcium hypochlorite it gives a brownish-red coloration, becoming reddish-brown, or, in dilute acetic acid solution, a violet coloration becoming brown, and forms a dark brown, flocculent precipitate.

3 : 5-Dibromo-*o*-quinonediazide, prepared by the action of nitrous acid on the dibromoaminophenol, crystallises from ether in glistening, orange-yellow prisms, or from light petroleum in compact, yellow needles, m. p. 130° (decomp.), and can be recrystallised from water, but decomposes on prolonged boiling; it couples with the naphthols or resorcinol in alkaline, or with α-naphthylamine in acetic acid solution. When boiled with hydrobromic acid and copper powder, the quinonediazide yields 2 : 3 : 5-*tribromophenol*, $C_6H_2Br_3{\cdot}OH$, which crystallises from light petroleum in glistening needles, m. p. 91·5—92·5°, is readily volatile in a current of steam, gives a brownish-violet coloration with alcoholic ferric chloride, and forms a voluminous, crystalline precipitate (2 : 3 : 4 : 5-tetrabromophenol?) with bromine water.

G. Y.

3 : 6-Dihydroxyquinonebisdiazoanhydride.

Franz Henle (*Annalen*, 1906, **350**, 344—367).—The substance obtained by Nietzki and Benckiser (Abstr., 1885, 779, 1127) as a residue on dissolving crude triquinoyl in sulphurous acid, and considered by these authors to be di-iminodiquinoyl, is now shown to be 3 : 6-dihydroxyquinonebisdiazoanhydride,



$$N\begin{matrix}\diagup O{\cdot}C{\cdot}CO{\cdot}C{\cdot}N \diagdown \\ \diagdown\!\!\diagdown N{\cdot}C{\cdot}CO{\cdot}C{\cdot}O \diagup\!\!\diagup\end{matrix}N$$

This, like the diazo-anhydride of tetronic acid, as a colourless *syn*diazoanhydride resembles ethyl diazoacetoacetate anhydride (Wolff, Abstr., 1903, i, 203), whilst on the other hand it forms a sulphonate as does the yellow *o*-diazophenol.

3 : 6-Dihydroxyquinonebisdiazoanhydride is obtained also as an insoluble residue when crude triquinoyl is extracted with aqueous sodium chloride, or in a 70—80% yield by the action of sodium nitrite on diaminotetrahydroxybenzene hydrochloride in 80% sulphuric acid solution; it crystallises slowly from nitric acid, D 1·4, in long, white prisms, detonates at 128°, becomes yellow on exposure to light, is decomposed by prolonged boiling with water, forming a cherry-red solution, and yields diaminotetrahydroxybenzene hydrochloride when reduced with stannous chloride and fuming hydrochloric acid. In sodium carbonate solution the bisdiazoanhydride couples with R-salt, β-naphthol, or resorcinol, but not with phenol, giving an intense violet-red coloration, which becomes blue and fluorescent on addition of dilute sodium hydroxide, red on addition of acetic acid, and is destroyed by hot sulphuric acid.

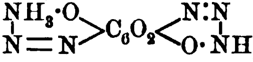
Tetrasodium 3 : 6-*dihydroxyquinonebisdiazosulphonate*,

$$C_6O_2(ONa)_2(N_2\cdot SO_3Na)_2,3H_2O,$$

formed with development of heat by the successive action of sodium hydrogen sulphite and sodium hydroxide on the bisdiazoanhydride, crystallises in orange-yellow leaflets, loses $3H_2O$ slowly in a vacuum over sulphuric acid, is very hygroscopic when anhydrous, and is decomposed, evolving gas when heated with water or dilute acids.

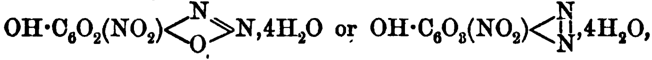
With an excess of aniline, the bisdiazoanhydride forms an *additive* compound, probably $C_6O_2(OH)_2(N_2\cdot NHPh)_2$, which is obtained as a dark red, crystalline powder, and decomposes into its generators slowly over sulphuric acid in a vacuum, more quickly when treated with organic solvents or acids. A similar *compound* is obtained on adding the bisdiazoanhydride to fused α-naphthylamine.

The action of concentrated aqueous ammonia on the bisdiazoanhydride leads to the formation of 3 : 6-*dioxyquinonebistriazen*,



$\begin{array}{l}NH_3\cdot O\\ \mid\\ N{=}N\end{array}\!\!>C_6O_2<\!\!\begin{array}{l}N{:}N\\ \quad\mid\\ O\cdot NH_3\end{array}$ (?), which crystallises in colourless prisms, m. p. 167°, decomposes above its melting point, and detonates when quickly heated. It is decomposed by aqueous sodium hydroxide, and when treated with concentrated aqueous or methyl-alcoholic hydrochloric acid or with hydrogen chloride in ethereal solution, evolves 4N and yields a *substance*, $C_6H_8O_4N_2Cl_2,2H_2O$.

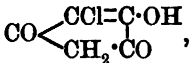
5-*Nitro*-3 : 6-*dihyroxyquinonediazoanhydride*,



$$OH\cdot C_6O_2(NO_2)<\!\begin{array}{c}N\\ \\ O\end{array}\!\!>N,4H_2O \text{ or } OH\cdot C_6O_3(NO_2)<\!\begin{array}{c}N\\ \|\\ N\end{array}\!,4H_2O,$$

prepared by the action of nitrosulphuric acid on 5-nitro-2-aminotetrahydroxybenzene hydrochloride in cooled 80% sulphuric acid solution, crystallises in lemon-yellow leaflets or long, thin needles, m. p. 70°, decomposes above 100° or when heated with a solvent, and detonates when heated rapidly; it is decomposed by concentrated aqueous ammonia or alkali hydroxides, but with dilute sodium carbonate and dilute ammonia forms highly explosive, yellow *salts*.

When treated with ethereal ammonia, 4 : 6-dibromo-2-diazophenol is partially decomposed evolving gas, whilst 4 : 6-dinitro-2-diazophenol forms a voluminous, red *product* which decomposes slowly in contact with ethereal ammonia, rapidly when exposed to air.

Chlorotriketocyclopentane,  $\mathrm{CO}<\begin{array}{l}\mathrm{CCl{=}C\cdot OH}\\ \qquad | \\ \mathrm{CH_2\cdot CO}\end{array}$ $,H_2O$, is formed when 3 : 6-dihydroxyquinonebisdiazoanhydride is boiled with 20% hydrochloric acid; it crystallises from moist chloroform in nodular aggregates of colourless needles, m. p. 72—74°, loses H_2O over sulphuric acid in a vacuum or when boiled with chloroform and calcium chloride, forming a white, hygroscopic, crystalline powder, m. p. 119°. It is a strong monobasic acid, is decomposed by concentrated alkali hydroxides, reduces ammoniacal silver solutions, and behaves towards bromine and potassium permanganate as an unsaturated substance, The *sodium*, $C_5H_2O_3ClNa,\frac{1}{2}H_2O$, and *ammonium*, $C_5H_2O_3Cl\cdot NH_4$, salts are described. The *acetate*, $C_7H_5O_4Cl$, forms colourless crystals, m. p. 57°; the *semicarbazone*, $C_6H_6O_3N_3Cl$, is obtained as an infusible, white, crystalline precipitate. When heated with bromine water, chlorotriketo*cyclo*pentane is converted into chloropentabromoacetone, m. p. 99° (m. p. 92°, Hantzsch, Abstr., 1889, 854). G. Y.

Hexanitroazobenzene. EUGÈNE GRANDMOUGIN and H. LEEMANN (*Ber.*, 1906, **39**, 4384—4385).—*Hexanitrohydrazobenzene*, prepared either by heating picrylhydrazine and picryl chloride for four hours at 120° or by heating an alcoholic solution of picryl chloride (2 mols.), hydrazine hydrate (1 mol.), and potassium hydroxide (3 mols.), forms bright yellow needles, m. p. 201°. The *monopotassium* salt dissolves in acetone to a deep red solution whilst the solution of the *dipotassium* salt is blue. *Hexanitroazobenzene*, prepared by the oxidation of the above compound with nitric acid, D 1·3, crystallises from glacial acetic acid in red prisms, m. p. 215°. W. R.

Anthranil. X. A New Reduction Product of *o*-Nitrobenzaldehyde. EUGEN BAMBERGER (*Ber.*, 1906, **39**, 4252—4276. Compare Bamberger and Elger, Abstr., 1904, i, 93; Heller, Abstr., 1906, i, 585).—In the reduction of *o*-nitrobenzaldehyde a new intermediate product has been found to be formed between *o*-hydroxylaminobenzaldehyde and anthranil.—[With E. W. REMMERT.]—If *o*-nitrobenzaldehyde is shaken with ether and aqueous ammonium chloride in a freezing mixture, while zinc dust is added gradually, there is formed a *product*,

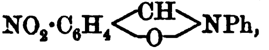
$$C_{14}H_{12}O_5N_2,$$

which for the present is termed *agnotobenzaldehyde*. It may have the constitution $NO_2\cdot C_6H_4\cdot CH(OH)\cdot N(OH)\cdot C_6H_4\cdot COH$ or

$$O[N(OH)\cdot C_6H_4\cdot COH]_2\,;$$

of these the latter is preferred. It crystallises in glistening, white needles, m. p. 94° if heated slowly from 65°, or 98·5—99° if heated rapidly from 85°, and decomposes slowly at the ordinary temperature, more quickly when treated with cold, dilute sulphuric acid or when boiled with water. It gives with alcoholic copper acetate a deep brown coloration rapidly becoming a dirty green, cuprous oxide being precipitated, reduces Fehling's solution, and when treated with 17% aqueous sodium hydroxide and ice becomes orange-red changing to yellow, and forms *o*-azoxybenzaldehyde, *o*-azobenzoic acid, *o*-nitrobenzaldehyde, *o*-nitrobenzyl alcohol, *o*-nitrobenzoic acid, traces of *o*-aminobenzaldehyde, and 2-*carboxybenzeneazoxy*-2′-*benzyl alcohol.*

Agnotobenzaldehyde does not form an *N*-aldoxime ether, whereas *o*-nitrobenzaldehyde condenses with phenylhydroxylamine, forming the N-*aldoxime ether*,



$NO_2{\cdot}C_6H_4{<}\overset{CH}{\underset{O}{}}{>}NPh$, which crystallises in slender, yellow needles, m. p. 93·5°.

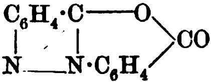
When reduced with aluminium amalgam and water in presence of ether, agnotobenzaldehyde yields anthranil and *o*-aminobenzyl alcohol; with phenylhydrazine in cooled pyridine solution it forms *o*-nitrobenzaldehydephenylhydrazone, m. p. 156·5—157°, together with the product $C_{13}H_{13}ON_3$, obtained by Buhlmann and Einhorn by the action of phenylhydrazine on anthranil (Abstr., 1901, i, 94).

o-Azoxybenzaldehyde, $ON_2(C_6H_4{\cdot}COH)_2$ (compare Bamberger and Demuth, Abstr., 1902, i, 95), crystallises from alcohol in golden-yellow needles, m. p. 118·5—119° when rapidly heated from 110°, intumesces at 130—140°, and yields a sublimate of slender needles; it reduces silver nitrate only slowly in ammoniacal solution, but rapidly in presence of sodium hydroxide. The *diphenylhydrazone*,

$$ON_2(C_6H_4{\cdot}CH{:}N_2HPh)_2,$$

crystallises in light orange needles, m. p. 185·5—186° (decomp.).

The action of direct sunlight on *o*-azoxybenzaldehyde in acetone solution leads to the formation of the *lactone* of *o*-indazolylbenzoic acid,



which crystallises in lemon-yellow needles with bronze lustre, m. p. 295°. The lactone is formed also together with *o*-azobenzoic acid (Maier, Abstr., 1902, i, 192) by oxidation of *o*-azobenzaldehyde with chromium trioxide in glacial acetic acid solution.

2′-*Benzyl alcohol-azoxy*-2-*benzoic acid*,

$$OH{\cdot}CH_2{\cdot}C_6H_4{\cdot}N_2O{\cdot}C_6H_4{\cdot}CO_2H,$$

crystallises from water or alcohol in strongly refracting, small, hard, almost colourless prisms, m. p. 160—161°, forms a lemon-yellow solution in water or alcohol and has an acid reaction. The *silver*,

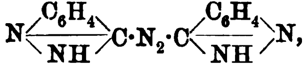
$$C_{14}H_{11}O_4N_2Ag,$$

copper, $(C_{14}H_{11}O_4N_2)_2Cu$, and *lead*, $(C_{14}H_{11}O_4N_2)_2Pb$, salts are described.

2′-*Benzaldehydeazoxy*-2-*benzoic acid*, $CO_2H{\cdot}C_6H_4{\cdot}N_2O{\cdot}C_6H_4{\cdot}COH$, prepared by oxidation of the alcohol with potassium dichromate in dilute sulphuric acid solution, crystallises in golden-yellow needles, m. p. 179—180° (decomp.), and reduces silver nitrate and Fehling's solutions on prolonged boiling in presence of sodium hydroxide. The *phenylhydrazone*, $CO_2H{\cdot}C_6H_4{\cdot}N_2O{\cdot}C_6H_4{\cdot}CH{:}N_2HPh$, crystallises in orange-red leaflets with bronze lustre, m. p. 156°; the *sodium* salt forms golden-yellow leaflets.

On prolonged boiling with potassium dichromate in dilute sulphuric acid solution, 2′-benzyl alcohol-azoxy-2-benzoic acid or its aldehyde yields *o*-azoxybenzoic acid. G. Y.

Oxidation of Aminoindazoles and a Remarkable Method of Formation of Dichloroindazole. EUGEN BAMBERGER and S. WILDI (*Ber.*, 1906, 39, 4276—4285).—Whilst indazoles containing an amino-group in the pyrazole nucleus are converted by various oxidising agents in acid solution into 4-hydroxy-β-phenotriazine (Bamberger and v. Goldberger, Abstr., 1899, i, 170; Bamberger, *ibid.*, 543), 3-aminoindazole is oxidised by potassium ferricyanide or atmospheric oxygen in alkaline solution, yielding 3 : 3′-azoindazole,



$$N\left\langle\begin{matrix}C_6H_4\\NH\end{matrix}\right\rangle C\cdot N_2\cdot C\left\langle\begin{matrix}C_6H_4\\NH\end{matrix}\right\rangle N,$$

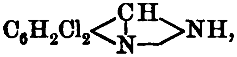
ammonia, and a small amount of a brown *acid*.

3 : 3′-*Azoindazole*, $C_{14}H_{10}N_6,C_2H_6O$, crystallises from alcohol in dark red, glistening needles with intense green lustre, m. p. 229·5° (corr.), and gives a light blood-red coloration with concentrated sulphuric acid. It dissolves in aqueous alkali hydroxides, forming a bluish-red solution, dyes silk and wool in an acid bath a rose colour, and is readily reduced by zinc dust, forming 3-aminoindazole. The *nitrate*, $C_{14}H_{10}N_6,2HNO_3$, forms slender, red needles with green lustre. The *diacetyl* derivative, $N_2(C_7H_4N_2Ac)_2$, crystallises in slender, orange needles, m. p. 210° (corr.), gives with concentrated sulphuric acid a dark blue coloration becoming red on addition of water, and is readily hydrolysed by dilute alkali hydroxides. The *dibenzoyl* derivative, $C_{28}H_{18}O_2N_6$, crystallises in glistening needles, m. p. 195—196° (corr.).

Azoindazole reacts with aniline at the laboratory temperature, forming 3-aminoindazole, 3-benzeneazoindazole, and a *substance* (*azoindazole hydrate*?), $C_{14}H_{12}ON_6$, which crystallises in glistening, bronze needles, m. p. 338·5°.

3-Benzeneazoindazole, m. p. 190·5—192·5° (corr.), is identical with the dye obtained by Bamberger (*loc. cit.*) by the action of diazobenzene chloride on indazole.

3-Amino-5 : 7-dimethyl- and 3-amino-5-methyl-indazole are oxidised by atmospheric oxygen in aqueous alkaline solution in the same manner as is 3-aminoindazole. Along with the corresponding *dye*, 3 : 3′-*azo*-5 : 5′-*dimethylindazole* forms an *acid* which crystallises in glistening, colourless needles, m. p. about 160°. The red coloration, formed on shaking these substances with air in alkaline solution, constitutes an extremely delicate reaction for 3-aminoindazoles.

Dichloroindazole,  $C_6H_2Cl_2\left\langle\begin{matrix}CH\\N\end{matrix}\right\rangle NH$, is formed together with indazole, a *substance* which is soluble in cold dilute sodium hydroxide, and a sparingly soluble, indifferent *substance* (trichloroindazole?) by the action of alkali hydroxides on an *o*-diazotoluene salt. It crystallises in matted, white needles, m. p. 242—242·5°, sublimes in woolly needles, is only slightly volatile in a current of steam, has feeble basic properties, and is soluble in boiling dilute sodium hydroxide (compare Abstr., 1899, i, 720).

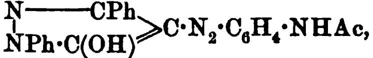
G. Y.

Diazo-compounds from *p*-Phenylenediamine with Heterocyclic Side-chains. Carl Bülow and Fritz Busse (*Ber.*, 1906, 39, 3861—3868. Compare Abstr., 1906, i, 717).—*Ethyl* p-*acetylaminobenzeneazobenzoylacetate*, $NHAc\cdot C_6H_4\cdot N_2\cdot CH(COPh)\cdot CO_2Et$, obtained by condensing a diazo-salt of acetyl-*p*-phenylenediamine with an alcoholic solution of ethyl benzoylacetate, crystallises from alcohol in yellow needles, m. p. 95·5°. The ester reacts with an aqueous alcoholic ammonia solution, yielding the *amide*,

$$NHAc\cdot C_6H_4\cdot N_2\cdot CH(COPh)\cdot CO\cdot NH_2,$$

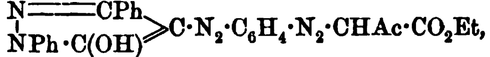
in the form of pale yellow needles, m. p. 252°.

Phenylhydrazine reacts with an acetic acid solution of the ester, yielding 4-p-*acetylaminobenzeneazo*-1 : 3-*diphenyl*-5-*pyrazolone*,



$$\left.\begin{matrix}N\text{———}CPh\\ NPh\cdot C(OH)\end{matrix}\right>C\cdot N_2\cdot C_6H_4\cdot NHAc,$$

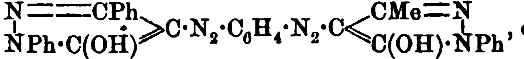
which crystallises from dilute acetic acid in red needles, readily soluble in most organic solvents and in dilute alkalis, but insoluble in ether, light petroleum, or water. 4-p-*Aminobenzeneazo*-1 : 5-*diphenyl*-5-*pyrazolone*, $C_{21}H_{17}ON_5$, obtained by hydrolysing the acetyl derivative with sodium hydroxide solution, crystallises from alcohol in reddish-brown needles, m. p. 208—209°. The diazo-chloride derived from this amine reacts with an alcoholic solution of ethyl acetoacetate in the presence of sodium acetate, yielding *ethyl* 1 : 3-*diphenyl*-5-*pyrazolone*-4-*azobenzene*-p-*azoacetoacetate*,



$$\left.\begin{matrix}N\text{===}CPh\\ NPh\cdot C(OH)\end{matrix}\right>C\cdot N_2\cdot C_6H_4\cdot N_2\cdot CHAc\cdot CO_2Et,$$

which crystallises from alcohol in pale red needles, m. p. 195—196° (decomp.).

1 : 3-*Diphenyl*-5-*pyrazolone*-4-*azobenzene*-p-4′-*azo*-1′-*phenyl*-3′-*methyl*-5′-*pyrazolone*,



$$\left.\begin{matrix}N\text{===}CPh\\ NPh\cdot C(OH)\end{matrix}\right>C\cdot N_2\cdot C_6H_4\cdot N_2\cdot C\left<\begin{matrix}CMe\text{=}N\\ C(OH)\cdot NPh\end{matrix}\right.,$$

obtained by the action of phenylhydrazine on the preceding compound, may be recrystallised from hot benzene or by solution in hot nitrobenzene and precipitation with acetic acid. It forms reddish-brown plates with a green, metallic lustre, m. p. about 270° (decomp.).

The constitution of the last-mentioned compound has been established by its formation by the following stages: 1-phenyl-3-methyl-5-pyrazolone-4-azobenzenediazo-chloride —> *ethyl* 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*azobenzene*-p-4′-*azobenzoylacetate*, $C_{27}H_{24}O_4N_6$, m. p. 203° —> 1′-phenyl-3′-methyl-5′-pyrazolone-4-azobenzene-*p*-4′-azo-1 : 3-diphenyl-5-pyrazolone.

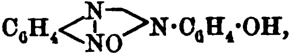
J. J. S.

Reduction of Nitroazo-compounds with Sodium Hyposulphite. Eugène Grandmougin (*Ber.*, 1906, **39**, 3929—3932. Compare Abstr., 1906, i, 716, 967).—The reduction of nitroazo-compounds with sodium hyposulphite does not always proceed normally; *o*-nitroazo-compounds in particular are only partially reduced, whilst azoimino-oxides are also formed.

Benzeneazosalicylic acid undergoes normal reduction with formation of aniline and 5-aminosalicylic acid.

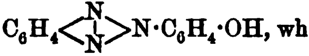
m-Nitrobenzeneazosalicylic acid is reduced to aminosalicylic acid and *m*-phenylenediamine, whilst *p*-nitrobenzeneazosalicylic acid yields aminosalicylic acid and *p*-phenylenediamine.

o-Nitrobenzeneazophenol, on reduction with sodium hyposulphite, forms p-*hydroxyphenylazoiminobenzene oxide*,



$$C_6H_4\left<\begin{matrix}N\\ NO\end{matrix}\right>N\cdot C_6H_4\cdot OH,$$

which crystallises in colourless needles, m. p. 232—233°; its *acetyl* derivative separates from dilute alcohol in needles, m. p. 176°. When *p*-hydroxyphenylazoiminobenzene oxide is reduced by stannous chloride, it forms *p*-hydroxyphenylbenzotriazole,



$C_6H_4\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle N\cdot C_6H_4\cdot OH$, which separates from alcohol in colourless needles, m. p. 219°. A. McK.

Digestion of Egg and Serum Proteids by Papain. D. JONESCU (*Biochem. Zeit.*, 1906, **2**, 177—187).—Digestion of the proteids named with papain stops short at peptone; amino-acids are not found. Coagulated egg-white and fibrin are not digested at all. The influence of temperature is discussed; reversibility of action was not discovered, and the questions of pro-ferment and activation suggested.
W. D. H.

Albumin Extracted from Fishes' Eggs, and a comparison of it with the Vitellin of Hens' Eggs. LOUIS HUGOUNENQ (*Compt. rend.*, 1906, **143**, 693—694. Compare Abstr., 1906, i, 324).—The albumin extracted from the eggs of *Clupea harengus* and called *clupeovin* by the author, yields on hydrolysis arginine, histidine, lysine, tyrosine, leucine, aminovaleric acid, alanine, serine, phenylalanine, and aspartic acid; it follows therefore that the vitellin obtained from the egg-albumin of birds or fishes is formed of the same compounds associated in comparable if not almost identical proportions (Abstr., 1906, i, 85, 776). M. A. W.

Occurrence of *iso*Leucine in Casein. R. WEITZENBÖCK (*Monatsh.*, 1906, **27**, 831—837).—The first phosphotungstate precipitate, obtained from a large amount (3 kilos) of casein, contains leucine, *iso*leucine (Ehrlich, Abstr., 1904, i, 56), and small amounts of arginine, histidine, lysine, and probably aminovaleric acid and phenylalanine.

If the phosphotungstate precipitate is distilled with aqueous potassium hydroxide, and the distillate evaporated with hydrochloric acid and redistilled with aqueous baryta, leucine and *iso*leucine are present in the final distillate and can be separated by Ehrlich's method. G. Y.

The Homogeneous Nature of Hæmatin and Attempts to Remove Iron from Blood-colouring Matter. RICHARD VON ZEYNEK (*Zeit. physiol. Chem.*, 1906, **49**, 472—481. Compare Abstr., 1900, i, 711).—Hæmin obtained by the pepsin-hydrochloric acid method closely resembles hæmin obtained by other methods. It may be crystallised from acetic acid and the analytical data agree fairly well with the formula $C_{34}H_{33}O_4N_4ClFe$.

When the blood-colouring matter is left in contact with pepsin-hydrochloric acid for some months, the yield of crystallised hæmin is small, and considerable amounts of residues are left in the pyridine-chloroform solutions, but the percentage of iron is not reduced. Hæmin prepared by the pepsin-hydrochloric acid method is more readily decomposed by dilute acid or by water at 180° than is ordinary hæmin. It is also more readily decomposed when a feeble electric current is passed through its alkaline solution.

When a suspension of hæmin in sulphurous acid solution is exposed to light, the aqueous liquid becomes purple-red in colour and shows the characteristic bands of hæmatoporphyrin. The iron has been removed from the hæmin and is contained in the solution in the ionic state.

J. J. S.

Nucleic Acids. XI. Phœbus A. Levene and John A. Mandel (*Zeit. physiol. Chem.*, 1906, 49, 262—265. Compare Abstr., 1906, i, 468).—The nuclein substance obtained from the egg of the shell-fish, *Gadas æglefinus*, appears to be a mixture of ichthulic and nucleic acids. It yields on hydrolysis the purine bases, guanine and adenine, the pyrimidine bases, cytosine and uracil. It gives a positive orcinol reaction, but the yield of lævulic acid is very small.

W. D. H.

Composition of Nucleic Acids of Thymus and Herring-roe. Hermann Steudel (*Zeit. physiol. Chem.*, 1906, 49, 406—409. Compare Abstr., 1906, i, 125).—The four nitrogenous components of these nucleic acids seem to be present in molecular proportion. They are guanine, adenine, cytosine, and thymine. W. D. H.

Cleavage of Gelatin. Phœbus A. Levene and Wallace A. Beatty (*Zeit. physiol. Chem.*, 1906, 49, 247—251, 252—261. Compare Abstr., 1904, i, 357; 1906, i, 469).—The following are the percentage amounts of cleavage products obtained from gelatin: glycine, 19·25; alanine, 3·00; leucine, 6·75; α-proline, 6·25; oxyproline, 6·4; phenylalanine, traces; aspartic acid, absent, and glutamic acid, 1·75.

W. D. H.

Cerebrone. III. F. Kitagawa and Hans Thierfelder (*Zeit. physiol. Chem.*, 1906, 49, 286—292. Compare Abstr., 1906, ii, 183).—A new method for the separation of cerebrone is described. In a 5°/₀ solution in 75°/₀ chloroform, $[\alpha]_D^{50} + 7·6$. Sphingosine was the name given by Thudichum to a basic cleavage product of his phrenosin. In the present research a base with the formula

$$C_{19}H_{39}O_2N$$

was prepared, but its relationship to sphingosine is at present uncertain. W. D. H.

Diffusion of Enzymes through Cellulose Membranes. Alb. J. J. Vandevelde (*Biochem. Zeit.*, 1906, 1, 408—412).—Leune's cellulose membrane and pig's intestinal membrane were employed. Invertase does not diffuse through the former, but easily diffuses through the latter. Maltase, rennet, and blood-catalase behave like invertase. Zymase diffuses through neither, but the isolated enzyme was not employed, only yeast cells. W. D. H.

Organic Chemistry.

A New Octane [δ-Methylheptane]. LATHAM CLARKE (*Ber.*, 1907, 40, 352—355).—This is the fourth octane to be prepared; the three at present known are *n*-octane, di-*iso*butyl (βε-dimethylhexane), and γ-methylheptane. The synthesis was accomplished by first preparing *ethyl β-amylacetoacetate*, $CH_3·CO·CH(CHMePr^{\alpha})·CO_2Et$, from β-iodopentane and ethyl sodioacetoacetate; the oil, b. p. 226°, has a characteristic almond-like odour. On hydrolysis with 10% potassium hydroxide, *δ-methyl-β-heptanone*, $CH_3·[CH_2]_2·CHMe·CH_2·CO·CH_3$, is obtained as an oil, b. p. 156°. The ketone, on being reduced with sodium in the presence of ether and water, gives *δ-methyl-β-heptanol*, $CHMe·Pr^{\alpha}·CH_2·CHMe·OH$, an oil, b. p. 168°, and a pinacone, b. p. 285—290°. β-Iodo-δ-methylheptane was obtained, but not isolated, by the reduction of the alcohol by hydrogen iodide at 100°, and on replacing the iodine by means of zinc and hydrochloric acid *δ-methylheptane* was obtained as a colourless, almost odourless, mobile oil, b. p. 118°. W. R.

Preparation of Tetra- and Hexa-chloroethanes from Acetylene. SALZBERGWERK NEU-STASSFURT (D. R.-P. 174068).—The direct addition of chlorine to acetylene takes place with explosive violence, carbon being eliminated and hydrogen chloride formed, owing to the great affinity of this halogen for hydrogen. The catalytic processes hitherto in vogue are not entirely satisfactory, but the difficulties of this chlorination are overcome by passing acetylene into sulphur chloride in the presence of iron powder or some iron compound. When the mixture is cooled, tetrachloroethane is produced, and when heated to boiling (138°), hexachloroethane is obtained. The former product is isolated by distillation alone or in steam, whilst the latter crystallises from hot sulphur chloride and is collected, and either sublimed, distilled, or recrystallised from alcohol.

When the absorption of acetylene slackens, the mixture is saturated with chlorine, and in this way, by alternating with acetylene and chlorine, the process is rendered continuous. In the absence of the catalyst, the sulphur chloride has no action on the acetylene.

G. T. M.

Preparation of Methyl and Ethyl Iodides. WEINLAND and K. SCHMID (D. R.-P. 175209).—Although dry potassium chloride yields methyl chloride on heating with methyl sulphate, yet potassium bromide and iodide when similarly treated do not undergo a like change, methyl bromide is not the exclusive product, and methyl iodide is not obtained by this process. It has now been found that by slowly adding methyl or ethyl sulphate to a warm concentrated aqueous solution of an alkali iodide, the alkyl iodide is produced quantitatively. G. T. M.

Application of the Principle of Partition. VIII. Constitution of the Hexyl Iodide obtained from Mannitol. ARTHUR MICHAEL and ROBERT N. HARTMAN (*Ber.*, 1907, **40**, 140—146. Compare Erlenmeyer and Wanklyn, *Zeitsch. Chem.*, 1863, **6**, 564; Combes and Le Bel, Abstr., 1893, i, 246).—From theoretical considerations, the conclusion is drawn that the hexyl iodide from mannitol contains a considerable amount of β-iodohexane, and a certain amount of γ-iodohexane, but little or no α-iodohexane. The amounts of the β- and γ-iodo-derivatives actually found were respectively 65—60% and 35—40%.

The hexyl iodide was prepared by Domac's method (Abstr., 1881, 1113), and purified by distillation under reduced pressure. It was transformed into the acetate by means of silver acetate and glacial acetic acid. One hundred and ten grams of hexyl iodide gave 18 grams of hexene and 42 grams of hexyl acetate, b. p. 150—158°.

The acetate on hydrolysis gave 26 grams of hexyl alcohol, b. p. 136—140°, which when oxidised by Lieben's method gave 17·8 grams of ketone. When analysed by the semicarbazide method, this indicated the presence of some 60% of β-hexanone. J. J. S.

αα-Dichloro*iso*propyl Alcohol and the Preparation of Dichloroacetaldehyde. ALFRED WOHL and H. ROTH (*Ber.*, 1907, **40**, 212—218. Compare Jocitsch and Faworsky, Abstr., 1899, i, 786; Fourneau and Tiffeneau, Abstr., 1905, i, 591; Höring, Abstr., 1905, i, 903; Oddo and Mameli, Abstr., 1904, i, 280).—The authors have attempted to prepare dichloro*iso*propyl alcohol by reduction of trichloro*iso*propyl alcohol, but unsuccessfully, as the reaction proceeds beyond the first stage. Reduction of the trichloro-alcohol by means of zinc dust and glacial acetic acid in cooled aqueous solution leads to the formation of αα-dichloropropylene, or by means of sodium and boiling absolute alcohol to the formation of ethyl α-ethoxypropionate, b. p. 73°/42 mm.

When treated with zinc ethyl in cooled ethereal solution in an atmosphere of carbon dioxide, dichloroacetone evolves gas and yields a mixture of chlorinated products, b. p. 35—50° and 50—57°/19 mm. The action of magnesium *tert.*-butyl bromide, prepared by slowly adding magnesium to *tert.*-butyl bromide in ethereal solution, on dichloroacetone leads to the formation of *iso*butylene.

Dichloroacetaldehyde is prepared in a 70·8% yield by heating dichloroacetal with benzoic anhydride and concentrated sulphuric acid at 170—180° and finally at 200°. When treated with magnesium methyl bromide in cooled ethereal solution it yields *dichloro*iso*propyl alcohol*, $OH\cdot CHMe\cdot CHCl_2$, b. p. 146—148°/765 mm. G. Y.

Synthesis of Alcohols by Means of Organomagnesium Compounds. III. MICHAEL I. KONOWALOFF, K. MILLER, and TIMTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, ii, 447—448. Compare Abstr., 1904, i, 496; Grignard, Abstr., 1900, i, 382).—*Methylethyl*tert.*-amylcarbinol* or *δ-hydroxy-γγδ-trimethylhexane*,

$$CMe_2Et\cdot CMeEt\cdot OH,$$

prepared by the action of methyl ethyl ketone on magnesium β-bromo-β-methylbutane, has m. p. 165—166°, D_0^{21} 0·8323, n_D^{21} 1·43407, is only sparingly soluble in water, but absorbs it rapidly and has the ordinary odour of a tertiary alcohol. In the synthesis of alcohols by Grignard's method, the ketone or aldehyde employed is often itself reduced to the corresponding alcohol; thus fenchone when treated with magnesium ethyl iodide yielded chiefly fenchyl alcohol, whilst *tert.*-bromobutane and pentane with benzophenone gave 38·5% of benzhydrol or its ester. Z. K.

Preparation of β-Glycols from Aldols by the Action of Organomagnesium Compounds. Adolf Franke and Moritz Kohn (*Monatsh.*, 1906, **27**, 1097—1128. Compare Abstr., 1905, i, 111; Lieben, Abstr., 1896, i, 403).—ββ-Dimethylbutane-αγ-diol, formed together with pentylene glycol, which on oxidation yields hydroxypivalic acid, by the action of magnesium methyl iodide (2 mols.) on formyl*iso*butaldol, is identical with Fossek's glycol (Abstr., 1884, 87).

ββ-Dimethylpentane-αγ-diol, formed by the action of magnesium ethyl iodide (2 mols.) on formyl*iso*butaldol, m. p. 60—63° (55°, Abstr., 1905, i, 111), b. p. 112—114°/11 mm., could not be completely purified.

The glycols described in this paper have been prepared by the action of organomagnesium compounds on aldols. Full details are given as to the methods of purification, which are mostly complicated and tedious.

γ-Phenyl-ββ-dimethylpropane-αγ-diol (Swoboda and Fossek, Abstr., 1891, 31) is formed together with diphenyl by the action of magnesium phenyl bromide on formyl*iso*butaldol.

[With Eugen Thiel.]—Acetaldol is obtained in a 55% yield by the action of aqueous potassium hydrogen carbonate on acetaldehyde below 10°; with magnesium methyl iodide it forms pentane-βγ-diol, b. p. 201—202°/748 mm. (Poray-Koschitz, Abstr., 1904, i, 363); the *diphenylcarbamate*, $C_{19}H_{22}O_4N_2$, forms a white powder, m. p. 141°.

The action of magnesium ethyl iodide on acetaldol leads to the formation of *hexane-βδ-diol*, $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CHEt{\cdot}OH$, which is obtained as a viscid oil, b. p. 103°/11 mm. or 210—211°/750 mm. (corr.). The *diphenylcarbamate*, $C_{20}H_{24}O_4N_2$, m. p. 144°; the *diacetate*, b. p. 101—102°/13 mm. or 211°/750 mm. (partial decomp.).

The product of the action of magnesium phenyl iodide on acetaldol yields on distillation diphenyl and *α-phenylbutane-αγ-diol*,

$$OH{\cdot}CHPh{\cdot}CH_2{\cdot}CHMe{\cdot}OH,$$

which forms a white, crystalline powder, m. p. about 73·5°, b. p. 162—164°/11 mm.; the *diacetate*, $C_{14}H_{18}O_4$, is a transparent, mobile liquid, b. p. 157°/10 mm., which decomposes partially when boiled under atmospheric pressure.

[With Karl Zwiauer.]—Propaldol is obtained from propaldehyde in a 70% yield by Lieben's method. It reacts with magnesium methyl iodide, forming *γ-methylhexane-βδ-diol*, $OH{\cdot}CHEt{\cdot}CHMe{\cdot}CHMe{\cdot}OH$, which is obtained as a colourless, viscid oil, b. p. 112·5°/9 mm.; the *diacetate*, $C_{11}H_{20}O_4$, forms a transparent, mobile liquid, b. p. 103·5—105·5°/11 mm.

δ-Methylheptane-γε-diol, $OH \cdot CHEt \cdot CHMe \cdot CHEt \cdot OH$, formed from propaldol and magnesium ethyl iodide, is obtained as a transparent, odourless liquid, b. p. 120—123°/14 mm.; the *diacetate*, $C_{12}H_{22}O_4$, is a mobile, transparent liquid, b. p. 112—113°/13 mm.

α-Phenyl-β-methylpentane-αγ-diol, $OH \cdot CHEt \cdot CHMe \cdot CHPh \cdot OH$, formed together with benzene and diphenyl from magnesium phenyl iodide and propaldol, is obtained as a transparent, extremely viscid substance, b. p. 169—173°/14 mm., which solidifies to a white mass when cooled with solid carbon dioxide and alcohol, and cannot be completely purified. The *diacetate*, $C_{16}H_{22}O_4$, is a mobile, transparent oil, b. p. 169·5—170°/14 mm., which has a pleasant odour. G. Y.

Aldol, Pentaerythrose, and the Action of Copper Acetate on the Hexoses. A. F. McLeod (*Amer. Chem. J.*, 1907, **37**, 20—50).—It has been shown by Tollens (Abstr., 1892, 127; 1893, 617) that considerable quantities of pentaerythritol can be obtained by the condensation of acetaldehyde (1 mol.) with formaldehyde (4 mols.). From a consideration of Nef's work, it is probable that this change is effected by the following successive reactions, involving the intermediate formation of hydracrylaldehyde, ββ′-dihydroxy*iso*butaldehyde, and pentaerythrose:

$$3OH \cdot CH\colon + H \cdot CH_2 \cdot CHO \longrightarrow OH \cdot CH_2 \cdot CH_2 \cdot CHO + OH \cdot CH\colon \longrightarrow$$
$$CH(CH_2 \cdot OH)_2 \cdot CHO + \colon CH \cdot OH \longrightarrow C(CH_2 \cdot OH)_3 \cdot CHO.$$
$$C(CH_2 \cdot OH)_3 \cdot CHO + \colon CH \cdot OH + 2H_2O \longrightarrow OH \cdot CH(OH)_2 + C(CH_2 \cdot OH)_3 \cdot CH_2 \cdot OH.$$

The present investigation has been carried out with the object of obtaining experimental proof that the condensation does take place in the stages indicated. It has been found that considerable quantities of pentaerythrose can be isolated, and indications have been obtained of the presence of relatively large amounts of ββ′-dihydroxy*iso*butaldehyde in the reaction product. Further, it is shown that mixtures of hydracrylaldehyde (1 mol.) and formaldehyde (2 mols.) in presence of traces of sodium hydroxide give an almost quantitative yield of pentaerythrose.

Experiments with acetaldehyde have shown that when this compound is left in contact at the ordinary temperature with solutions of sodium or calcium hydroxide of concentration below 0·1%, little or no condensation of the aldehyde occurs. The conditions under which the best yields of aldol and of crotonaldehyde can be obtained from acetaldehyde have been carefully studied. Acetaldehyde cannot be regenerated from aldol or crotonaldehyde by treatment with water, with very dilute alkalis, or with acids in sealed tubes at 100°. Under these conditions, aldol is readily transformed into crotonaldehyde, which, in turn, is converted into insoluble, yellow, volatile and non-volatile oils, and finally into aldehyde-resin.

The behaviour of acraldehyde and of hydracrylaldehyde towards alkalis has been investigated. Nef's statement (Abstr., 1905, i, 4) that crotonaldehyde is formed under these conditions is incorrect. The addition of traces of any alkali to a cold aqueous solution of acraldehyde results in the formation of an insoluble, amorphous polymeride, which decomposes at 94—95° and is analogous to that obtained by Nef by the action of barium hydroxide. These polymerides are neutral to sodium carbonate, but dissolve in 10% sodium hydroxide, and, after heating the solution for a short time at 100° and adding the calculated quantity of hydrochloric acid, yield a light brown, amorphous, substance of high melting point of about half the molecular weight of the original polymeride. On treating hydracrylaldehyde with sodium hydroxide, an insoluble polymeride is not formed in the cold, but on further treatment as in the previous case an insoluble polymeride is produced.

A quantitative estimation has been made of the amounts of cuprous oxide, carbon dioxide, and of formic, glycollic, and oxalic acids formed from 100 grams of *d*-dextrose, *d*-lævulose, or *d*-galactose when heated for eight hours on the water-bath with excess of copper acetate solution, but the results so far obtained are not sufficiently complete to enable a theory of the oxidation of hexoses to be put forward.

Experiments on the action of copper acetate solution on formaldehyde and on formic, glycollic, and oxalic acids have led to the following conclusions. The formic and carbonic acids obtained on oxidising the hexoses are not produced as the result of the decomposition of the oxalic acid formed as an intermediate product; the oxalic acid is not produced by an oxidation of glycollic acid, and the formation of carbonic acid is not due to the oxidation of formic acid.

E. G.

Synthesis of Natural Erythritol. ROBERT LESPIEAU (*Compt. rend.*, 1907, **144**, 144—146. Compare Abstr., 1905, i, 566).—The inactive erythrolactone previously described proves to be a racemic mixture, for on treating it in the presence of water with an equivalent quantity of brucine, and fractionally crystallising the product, a separation (probably incomplete) into brucine salts of rotatory power varying from $-25{\cdot}3°$ to $-34°$ is effected. The salt of rotatory power $-25{\cdot}3°$ gives a lactone of rotatory power $-35°$.

When the lactone is reduced by sodium amalgam (containing 2·6% of sodium) in a solution kept slightly acid, a syrup is obtained, which with phenylhydrazine gives, not erythrosazone, but a hydrazide identical with that obtained directly from the lactone. This syrup on keeping for three months deposits crystals identical with natural erythritol. The identity was established by the melting point, both alone and when mixed with the natural substance, by analysis, and by the production of a dibenzoylacetal, m. p. 195—196°, identical with that described by Fischer.

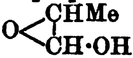
E. H.

Preparation of Alkyl Ethers. TH. VAN HOVE (*Bull. Acad. roy. Belg.*, 1906, 650—668).—By heating propyl alcohol or *iso*amyl alcohol with quinoline hydrochloride in closed tubes at 180° during six days, the author has obtained a mixture of products containing in each case the corresponding alkyl ether, alkyl chloride, and di- and tri-alkyl quinolines. The yield of pure propyl ether so obtained is 35% of the theoretical and of the *iso*amyl ethyl, 53%. When these alcohols are heated with quinoline alone, under the above conditions, no change occurs, whence it appears that the reaction, which takes place in the presence of quinoline hydrochloride, is due to the hydrolysis of this salt, the hydrochloric acid liberated forming the alkyl chloride, which then reacts in part with the alcohol and in part with the quinoline.

The alkylquinolines produced are separated by conversion into the picrates. *Dipropylquinoline*, b. p. 329° (corr.), yields a crystalline *picrate*, m. p. 189—190°. *Tripropylquinoline*, b. p. 348° (corr.), furnishes a crystalline *picrate*, m. p. 133°. A third amorphous basic product is obtained in this reaction, which also yields an amorphous picrate.

*iso*Amyl ether, b. p. 172·2°, has $D^{19\cdot2}$ 0·7767. From the mixture of bases obtained in the reaction with *iso*amyl alcohol, *diisoamylquinoline picrate* was obtained in slightly fluorescent tufts, m. p. 180°. In this reaction also a small amount of amylene is formed. T. A. H.

Ethyl *aa*-Dichloro*iso*propyl Ether and Dibromoacetaldehyde. Paul Freundler (*Compt. rend.*, 1907, **144**, 272—273).—By condensing dibromoacetaldehyde with magnesium methyl iodide, the author obtains a liquid denser than water, which he considers to be *aa-dibromoisopropyl alcohol.* This, however, is much less stable than the corresponding dichloro-compound obtained by Wohl (this vol., i, 170), undergoing partial decomposition when distilled, and its examination was not proceeded with.

Ethyl aa-dichloroisopropyl ether, $CHCl_2\cdot CHMe\cdot OEt$, formed as a by-product in the preparation of trichlorobutyric acetal (this vol., i, 13), is liquid, b. p. 145—146°. When heated with lead oxide and water in a sealed tube at 180—200°, it gives, not *β*-ethoxypropaldehyde, but a mixture of ethyl chloride (or ethyl alcohol) and lead propionate. It is suggested that the propionic acid arises from an internal transposition of the oxide,  $O<\begin{matrix}CHMe\\ |\\ CH\cdot OH\end{matrix}$, first formed, and that in any case the reaction contradicts Nef's theories on ethylidenic dissociation, whilst leading to the conclusion that it will not be possible to obtain lactaldehyde from an *aa*-dichloro-*β*-hydroxypropyl derivative as a starting point. E. H.

Butylene Nitrosite and Butylenediamine. Nicolaus J. Demjanoff (*Ber.*, 1907, **40**, 245—246).—When nitrous fumes are passed into a well-cooled ethereal solution of butylene, *butylene nitrosite*, $(C_4H_8O_3N_2)_2$, m. p. 103—104°, is precipitated in colourless, glistening prisms. From the ethereal residue, after reduction with tin and hydrochloric acid, butaldehyde and *butylenediamine*, $C_4H_8(NH_2)_2$, are obtained; the *hydrochloride*, *platinichloride*, *aurichloride*, and *picrate* of the latter are described. C. S.

Structure of Phosphorous Acid and its Derivatives. III. The Compounds of the Tervalent Phosphorus Derivatives with the Monohalogen Compounds of Copper. Alexander E. Arbusof (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, ii, 293—319. Compare this vol., i, 8).—Compounds of the type $CuX,P(OR)_3$ (where X stands for a halogen, R for Et, Ph, &c.) have been prepared by the gradual addition of an equivalent weight of copper halide to a weighed quantity of the phosphorous ester. On warming gently, the copper salt dissolves completely, and the solution crystallises immediately on cooling. Most of the salts thus formed are nearly insoluble in ether and ethyl and methyl alcohols, but they are readily soluble in chloroform and ethyl bromide. When exposed to the air they decompose, but they can be preserved indefinitely in a sealed tube in an atmosphere of carbon dioxide. Pure water has no action, whilst nitric acid oxidises them rapidly. The following compounds have been prepared. *Methyl* compounds, $CuCl,P(OMe)_3$, m. p. 190—192°; $CuBr,P(OMe)_3$, m. p. 180—182°; $CuI,P(OMe)_3$, m. p. 175—177°, can only be obtained at temperatures above 100°; at a low temperature the *substance*, $CuI,2P(OMe)_3$, m. p. 69—70°, is formed. *Ethyl* compounds are formed with greater difficulty. $CuCl,P(OEt)_3$ is a colourless, oily, unstable liquid which does not solidify at $-18°$; $CuBr,P(OEt)_3$, m. p. 27—28°; $CuI,P(OEt)_3$, m. p. 109—110°, are soluble in most organic solvents and are fairly stable in air. *Propyl* compounds, $CuI,P(OPr^{\alpha})_3$, m. p. 64—65°, the chloride and bromide are liquids difficult to purify; $CuCl,P(OPr^{\beta})_3$, m. p. 112—114°; $CuBr,P(OPr^{\beta})_3$, m. p. 149—150°; $CuI,P(OPr^{\beta})_3$, m. p. 184—185°, are soluble in most organic solvents, but are very unstable. *Phenyl* compounds, $CuCl,P(OPh)_3$, m. p. 95—96°, strongly refractive; $CuCl,2P(OPh)_3$, m. p. about 70°; $CuBr,P(OPh)_3$, m. p. 90·5—91·5°; $CuBr,2P(OPh)_3$, m. p. 73—74°; $CuI,2P(OPh)_3$, m. p. 73—76; $CuI,P(OPh)_3$, has not been obtained. iso*Butyl* compounds, $CuCl,P(OC_4H_9)_3$, prepared from the esters, $P(OC_4H_9)_3$, $P(OC_4H_9)_2\cdot OH$, was not obtained pure, but the corresponding *compounds*, $CuCl,P(OC_4H_9)_3,P(OPh)_3$, m. p. 54—55°, and $CuBr,P(OC_4H_9)_3,P(OPh)_3$, m. p. 58—59°, were prepared in a pure state.

Copper cyanide compounds have been prepared in an impure form; they exhibit a tendency to polymerise.

Triethylphosphine compounds, $CuCl,PEt_3$, m. p. 103—104°, and $CuI,2PEt_3$, m. p. 37—39°, are also described; the latter yields CuI,PEt_3 on heating.

Cuprous chloride, bromide, and iodide are also dissolved by the chloroanhydrides of phosphorous acids of the type $P(OR)Cl_2$ and by $P(OPh)_2Cl,P(OMe)_2Cl$, yielding crystalline *substances*.

Phosphorous tribromide or chloride reacts with cuprous bromide, forming the *substance*, $CuBr,PBr_3$, which could not be purified. It is insoluble in practically all solvents, and fumes strongly in air, yielding hydrogen bromide, cuprous bromide, and phosphorous acid.

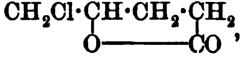
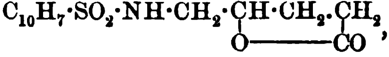
None of the derivatives of quinquevalent phosphorus reacts with the cuprous halogen compounds even when the substances are heated together for several days at 250°. Since neither phosphorous acid nor its acid derivatives form compounds with the cuprous halides, the phosphorus in this acid must be quinquevalent, and the structure of the acid must consequently be represented thus: $O{:}P{<}\begin{smallmatrix}(OH)_2\\ H\end{smallmatrix}$, and the derivatives, $O{:}P{<}\begin{smallmatrix}(OR)_2\\ H\end{smallmatrix}$.

Z. K.

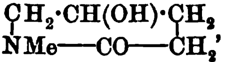
Acetyl Nitrate. Amé Pictet and Eugène Khotinsky (*Compt. rend.*, 1907, **144**, 210—212).—*Acetyl nitrate*, $CH_3\cdot CO\cdot O\cdot NO_2$, is obtained by dissolving nitric pentoxide in acetic anhydride; it is separated from excess of acetic anhydride by distillation under reduced pressure. If the mixture of acetyl nitrate and acetic anhydride is heated at the ordinary pressure, it undergoes a violent reaction at 60° with evolution of nitrous fumes and formation of tetranitromethane. Acetyl nitrate is a colourless, very mobile and hygroscopic liquid, b. p. 22°/70 mm., which fumes strongly in air and explodes violently on rapid heating. Analysis was effected by decomposition with water and estimation of the nitric and acetic acids formed. It reacts with alcohols, giving nitric or acetic esters according to the nature of the alcohol and the temperature. Aniline is converted into a mixture of molecular quantities of acetanilide and aniline nitrate. It is a very powerful nitrating agent towards aromatic compounds, benzene, toluene, anthracene, and thiophen being nitrated below 0°. With substituted benzenes, it has a tendency to give ortho- rather than para-nitro-derivatives. Thus toluene gives ten times as much *o*-nitro- as *p*-nitro-toluene. Acetanilide gives solely *o*-nitroacetanilide. E. H.

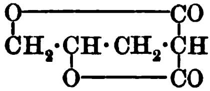
Hydrolysis of Sodium Palmitate. DAVID HOLDE and F. SCHWARZ (*Ber.*, 1907, **40**, 88—92. Compare Cohn, *Zeitsch. öffentl. Chem.*, 1905, **11**, 58; Abstr., 1906, ii, 58; Schwarz, Abstr., 1905, ii, 657).—The authors dispute Cohn's views on the hydrolysis of sodium palmitate. Palmitic acid (0·5—1 gram) was dissolved in 20 c.c. of aqueous *N*/2 alkali and the excess of alkali titrated with *N*/2 hydrochloric acid. It was shown that in aqueous solution 100% of palmitic acid cannot be formed in this manner by Cohn's method using phenolphthalein; that is, that the amount of excess of alkali and the amount of alkali, obtained by the hydrolysis of the salt, cannot be separately distinguished by this method. A. McK.

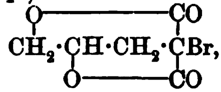
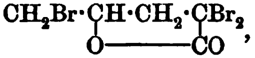
Occurrence of Dierucin in Rape Oil. C. L. REIMER (*Ber.*, 1907, **40**, 256—257. Compare Abstr., 1887, 233).—The separation of dierucin from rape oil occasionally occurs before refining (compare Marcusson, Abstr., 1906, i, 924; Lewkowitsch, this vol., i, 10), due possibly to a reaction between trierucin and water caused by fermentation. C. S.

Δ-Chloro-γ-valerolactone and some Related Compounds. HERMANN LEUCHS and OSKAR SPLETTSTÖSSER (*Ber.*, 1907, **40**, 301—310).—Whilst the chlorine of ethyl δ-chloro-γ-valerolactone-α-carboxylate is replaced by hydroxyl on warming with alkali (Traube and Lehmann, Abstr., 1901, i, 501), at 0° hydrolysis occurs, the chlorine for the most part remaining intact. The hydrolysis is effected much better, however, by hydrochloric acid, when a 90% yield of *δ-chloro-γ-valerolactone*,  $\begin{array}{l}CH_2Cl\cdot CH\cdot CH_2\cdot CH_2\\ \qquad\quad O\text{———}CO\end{array}$, is obtained as a colourless, almost odourless oil of b. p. 132—135°/12 mm., D^{18} 1·625, sparingly soluble in sodium carbonate. It dissolves in ammonia, forming a salt of chlorohydroxyvaleric acid, and when this solution is heated at 100° for one hour in a sealed tube, Emmerling's 3-hydroxy-6-piperidone is formed (Abstr., 1900, i, 16). *δ-(β)-Naphthalenesulphonamino-γ-valerolactone*,  $\begin{array}{l}C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot CH\cdot CH_2\cdot CH_2\\ \qquad\qquad\qquad\qquad\quad O\text{———}CO\end{array}$, is obtained in good

yield by heating the hydroxypiperidone for three hours with *N* sodium hydroxide (2 mols.) and then shaking the solution with β-naphthalenesulphonic chloride (2 mols.) dissolved in ether and 2 mols. more of the alkali. The lactone precipitated from its sodium salt by acid, crystallises from 50% alcohol in small rectangular plates, m. p. 143—144° (corr.); it dissolves easily in sodium hydroxide, but is insoluble in sodium carbonate.

3-*Hydroxy*-1-*methyl*-6-*piperidone*,  obtained by heating the chlorovalerolactone with aqueous methylamine in a sealed tube at 100°, is a thick, colourless oil, b. p. 193—195°/13 mm. It is characterised by forming the β-*naphthalenesulphonamino*-compound, $C_{16}H_{17}O_4NS$, crystallising in very small hexagonal plates, m. p. 82—83°.

The *dilactone*,  derived from γ-δ-dihydroxypropylmalonic acid, was isolated in small quantity from the product of the hydrolysis of ethyl chlorovalerolactonecarboxylate. If, however, the sodium salt in alcohol is heated in a closed tube at 100° for four hours, and the residue, left after evaporation of the alcohol, boiled with hydrochloric acid, a 14% yield of the dilactone is obtained; it forms colourless prisms, m. p. 179—180° (corr.). An ester cannot be prepared by heating it with an alcoholic solution of hydrogen chloride, nor is it soluble in alkali carbonates although it is easily soluble in alkali hydroxides. γδ-Dihydroxypropylmalonamide, obtained by heating the dilactone in a methyl alcohol solution of ammonia for twenty minutes, crystallises in slender prisms, m. p. 168—169° (corr.). That Traube and Lehmann's amide (m. p. 140°, *loc. cit.*) was impure is proved by the fact that both the dilactone and ethyl δ-hydroxy-γ-valerolactonecarboxylate give the same *bisphenylhydrazide*, $C_{18}H_{22}O_4N_4$, crystallising in colourless needles, m. p. 214° (corr. decomp.).

The *dilactone*,  of α-bromo-γδ-dihydroxypropylmalonic acid, prepared by heating a solution of the parent di-lactone in hydrobromic acid and bromine (2·2 mols.) in a sealed tube at 70° for one hour, crystallises from alcohol in hexagonal plates, m. p. 186—187° (corr.). When, however, the dilactone is heated with 4·4 mols. of bromine at 85° for four to five hours, *ααδ-tribromo-γ-valerolactone*,  is the product obtained, crystallising from aqueous alcohol in aggregates of needles, m. p. 84—85°.

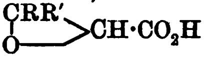
W. R.

Desmotropic Forms of Ethyl Acetoacetate at Low Temperatures. Hans Stobbe (*Annalen*, 1907, 352, 132—146).—By working at low temperatures (− 78° to − 64°) and using the characteristic red coloration which is obtained with ferric chloride when a definite quantity of the ketonic form of ethyl acetoacetate has changed into the enolic form, it has been possible to show that the velocity with which the ketonic form changes into the enolic is greatest in amyl alcohol, becoming smaller in the following alcohols in the order given: butyl, ethyl, methyl. For example, the red coloration appears in the case of amyl alcohol in thirty-nine secs., and in the case of methyl alcohol in fifty-six secs. after the addition of equal quantities of the ester to equal volumes of the respective alcoholic solutions at −78° containing ferric chloride in equal concentration. Since methyl alcohol possesses the greatest, and amyl alcohol the smallest, dielectric constant, it is obvious that the velocity of the change of the ketonic into the enolic form is greatest in the least dissociating medium. This result is contrary to that usually observed, with the one exception discovered by Dimroth (Abstr., 1905, i, 98). It is further shown, in agreement with Traube (Abstr., 1896, i, 593), but in contradiction to Brühl (Abstr., 1905, i, 407), that the proportion of the enolic form present is greater in alcoholic solutions than in the undissolved ester. W. H. G.

Determination of the Molecular Weight of Ethyl Acetoacetate in Freezing Chloroform. HANS STOBBE and ERNST MÜLLER (*Annalen*, 1907, **352**, 147—151).—The apparatus employed was a slightly modified form of the ordinary Beckmann's apparatus. The constant for chloroform, m. p. −62°, using ethyl benzoate as the solute, was found to be 499. The mol. weight found for ethyl acetoacetate showed it to be unimolecular in freezing chloroform. The authors therefore consider it probable that the ester is also unimolecular in alcoholic solutions at −78°, and that the slow rate with which the ketonic form of the ester changes into the enolic form at this temperature is not due to the formation of associated molecules, but merely to the low temperature (compare preceding abstract).

W. H. G.

New Synthesis of Ethyl γ-Chloroacetoacetate. M. PICHA [completed by RICHARD DOHT and S. WEISL] (*Monatsh.*, 1906, **27**, 1245—1249).—The action of aluminium amalgam on ethyl chloroacetate in presence of traces of alcohol leads with development of heat to the formation of ethyl γ-chloroacetoacetate, ethyl alcohol, and hydrogen chloride; the temperature of the reaction must not be allowed to rise above 120°. The γ-chloroacetoacetate is isolated in the form of its copper derivative, m. p. 163° (corr.) (168°: Lespieau, Abstr., 1899, i, 243), from which it is obtained by heating with dilute sulphuric acid. G. Y.

Preparation of ββ-Disubstituted Glycidic Acids. GEORGE DARZENS (D.R.-P. 174279).—Disubstituted glycidic acids having the general formula  $\begin{array}{l}CRR'\\ |\\ O\end{array}\!\!>CH\cdot CO_2H$ are readily obtained by condensing a ketone with a halogenated ethyl acetate in the presence of an alkaline reagent and then hydrolysing the resulting ester.

A mixture of methyl nonyl ketone and ethyl chloroacetate was treated with alcoholic sodium ethoxide; *ethyl methylnonylglycidate* thus obtained was distilled under reduced pressure, b. p. 165—170°/16 mm. *Ethyl* p-*tolylmethylglycidate* (b. p. 160—164°/16 mm.) and *ethyl benzylmethylglycidate* (b. p. 175—180°/16 mm.) were obtained respectively from *p*-tolyl methyl ketone and benzyl methyl ketone.

G. T. M.

Disubstituted Ethyl Acetoacetates and Malonates. HANS MEYER (*Monatsh.*, 1906, **27**, 1083—1096. Compare Abstr., 1906, i, 137, 358).—It has been shown previously that whilst methyl dimethyl- and methylethyl-malonates are converted into the corresponding diamides by the action of aqueous ammonia, methyl diethyl- and ethyl dimethyl-malonates remain unchanged. The action of ammonia on a number of other compounds of similar structure has been investigated with the object of throwing light on the relation of the stability of the system $CR'R''R'''\cdot CO_2Alk$ to the nature of the groups R', R'', and R'''.

Ethyl diethylacetoacetate remains unchanged when shaken with aqueous ammonia, but under the same conditions methyl dimethyl-, ethyl methylethyl-, and ethyl dimethyl-acetoacetates yield the corresponding amides.

Dimethylacetoacetamide, $COMe\cdot CMe_2\cdot CO\cdot NH_2$, m. p. 120—121°, crystallises from water or methyl alcohol.

Methylethylacetoacetamide, $COMe\cdot CMeEt\cdot CO\cdot NH_2$, separates from water in compact crystals, m. p. 123—124°.

The preparation described as commercial ethyl dimethylacetoacetate is usually the methyl ester (compare Peters, Abstr., 1891, 1097) which has the hydrolysis constant, $k = 2{\cdot}25$ at 25° (Goldschmidt and Oslan, Abstr., 1900, i, 373); the ethyl ester which must be prepared in two distinct stages, the intermediate ethyl methylacetoacetate being carefully fractionated, has the hydrolysis constant, $k = 0{\cdot}75$ at 25°.

Methyl diethylacetoacetate is hydrolysed partially by aqueous ammonia, but does not form the amide. On the other hand, methyl and ethyl ethylacetoacetates react with aqueous ammonia, forming the amide in a few hours, and ethyl benzylacetoacetate undergoes the reaction in two days, forming the amide, whilst methyl benzylacetoacetate, m. p. 291—293° (corr.), dissolves only in aqueous ammonia in six days, the product obtained on evaporation being identical with benzylmethylacetamide, m. p. 109°, prepared by the action of thionyl chloride and ammonia on benzylmethylacetic acid, m. p. 275—277°.

Ethyl diallylmalonate does not react with aqueous ammonia; the *methyl ester*, b. p. 235° (corr.), which is obtained on boiling the acid with methyl alcohol and sulphuric acid as an oil having an odour of pears, dissolves slowly in ammonia, and if evaporated after five days yields *diallylmalonamide*, $C(CH_2\cdot CH\colon CH_2)_2(CO\cdot NH_2)_2$, m. p. 201—202°; this gives the biuret reaction, decolorises potassium permanganate in sodium carbonate solution, and yields ammonia when treated with cold aqueous potassium hydroxide.

Ethyl methylpropylmalonate does not react with ammonia in aqueous solution; the *methyl ester*, b. p. 206—209°, yields *methylpropylmalonamide*, m. p. 182°, ammonium methylpropylmalonate, and *ethyl methylpropylmalonamate* (?), m. p. 67°, subliming.

Whilst ethyl benzylmethylmalonate does not react with aqueous ammonia, ethyl benzylmalonate rapidly forms the amide, m. p. 225°.

Methyl benzylmethylmalonate crystallises in large plates, m. p. 63°, has a pleasant odour, and is converted by ammonia into *benzylmethylmalonamide*, which crystallises in needles, m. p. 202—203°, and gives the biuret reaction.

Methyl cetylmalonate, m. p. 44°, crystallises from ether and does not react with ammonia.

Methyl triphenylacetate, m. p. 182°, is formed quantitatively by the action of diazomethane on the acid; it does not react with ammonia in aqueous solution at 120°, but when heated at 180° explodes.

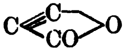
The action of aqueous ammonia on ethyl diethylmalonate for several months leads to the formation of a clear solution; this on evaporation leaves a syrupy residue, which when heated yields ethyl diethylmalonate and ammonium diethylmalonate in accordance with the equation: $2CO_2Et\cdot CEt_2\cdot CO_2NH_4 = CEt_2(CO_2Et)_2 + CEt_2(CO_2NH_4)_2$.

G. Y.

Carbon Suboxide. II. Otto Diels and Georg Meyerheim (*Ber.*, 1907, **40**, 355—363. Compare Abstr., 1906, ii, 227).—It has been found that carbon suboxide is formed when methyl, benzyl, or phenyl malonates, as well as ethyl malonate, are heated with phosphoric oxide; ethyl oxalacetate and ethyl methanetricarboxylate also yield it. The most interesting reaction studied, however, is that of malonic acid itself, as in addition to its giving acetic acid and carbon dioxide (the known fission of an *aa*-dicarboxylic acid), it also gives a 10—12% yield of carbon suboxide when heated at 140—150°, and serves as the most convenient method of preparing the compound. A description of the apparatus is given. Carbon suboxide has m. p. −107° and D_0^0 1·11.

When conducted through a heated constricted tube, carbon suboxide forms a characteristic metallic mirror like that given by arsine. At low temperatures the suboxide is stable, and the change into the dark red product at 0—15°, due to polymerisation, is hastened by traces of impurity. This polymeride or mixture of polymerides is very hygroscopic; with cold water, heat is developed, an eosin-red solution is formed, carbon dioxide being evolved at the same time. On heating the polymerised product, carbon monoxide, carbon dioxide, and carbon suboxide are obtained. Heating the suboxide to a higher temperature, or working with larger quantities, results in an evolution of carbon monoxide and dioxide; the residue, probably a complicated mixture, contains more carbon than the suboxide.

The authors consider that carbon suboxide is to be represented as a malonic anhydride, OC:C:CO, and not as the lactone of *β*-hydroxypropionic acid,

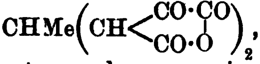


$C\ll\begin{matrix}C-\\CO\end{matrix}>O$ (Michael, Abstr., 1906, ii, 442).

Dehydracetic acid is formed when acetic anhydride is heated with phosphoric oxide.

W. R.

Action of Reducing Agents on Cholic Acid. Alfred Ekbom (*Zeitsch. physiol. Chem.*, 1906, **50**, 97—124).—Vahlen's conclusion (Abstr., 1897, i, 648) that deoxycholic acid is formed by the reduction of cholic acid with alkaline reducing agents has not been confirmed; in all cases unaltered cholic acid was obtained. It is probable that the acid used by Vahlen contained a reduction product. When heated with acetic acid or with zinc dust and acetic acid, cholic acid yields a mixture of mono- and diacetyl derivatives, which may be obtained as a flocculent precipitate on the addition of water. These acetyl derivatives do not give Mylius's reaction. J. J. S.

The Pyran Series. IV. H. Gault (*Bull. Soc. chim.*, 1907, [iv], 1, 40—48. Compare this vol., i, 148).—*Ethyl ethylidenebisoxalacetatehydrate*, $CHMe[CH(CO_2Et)\cdot CO\cdot CO_2Et]_2,H_2O$, m. p. about 112°, obtained by condensing acetaldehyde with ethyl oxalacetate as already described (*loc. cit.*), crystallises from dilute alcohol, and gives a coloration with ferric chloride on warming. The anhydrous ester could not be isolated. The *monophenylhydrazone*, m. p. 135°, crystallises from alcohol; the *monosemicarbazone*, m. p. 185°, crystallises from boiling water. Cold sulphuric acid hydrolyses the hydrated ester, forming *ethylidenebisoxalacetic dianhydride*,  $CHMe\left(CH<\begin{matrix}CO\cdot CO\\ |\quad\ \ |\\ CO\cdot O\end{matrix}\right)_2$, which forms a very soluble hydrate with cold water, and on warming with water decomposes, evolving 2 mols. of carbon dioxide and forming diketomethylpimelic acid; a similar decomposition of the dianhydride is brought about by alcohol, whilst aniline furnishes a dianilide which decomposes on contact with water, forming the dianilide of diketomethylpimelic acid. Boiling dilute mineral acids convert the hydrated ester directly into diketomethylpimelic acid.

Ethyl propylidenebisoxalacetate hydrate, m. p. 118°, is prepared similarly from propaldehyde and ethyl oxalacetate. The anhydrous ester could not be isolated. The *monophenylhydrazone*, m. p. 129°, crystallises from dilute alcohol, and the *monosemicarbazone*, m. p. 160°, separates in crystals from the same solvent. *Propylidenebisoxalacetic dianhydride*, m. p. about 170° (decomp.), obtained on treating the hydrated ester with cold sulphuric acid and with cold water, yields the corresponding unstable tetra-acid, which rapidly decomposes, yielding diketoethylpimelic acid. With alcohol the dianhydride yields ethyl diketoethylpimelate and with aniline the corresponding dianilide, which readily decomposes, forming the dianilide of diketoethylpimelic acid. The latter acid is produced in minute quantities when the hydrated ester is boiled with dilute mineral acids.

Ethyl heptylidenebisoxalacetate hydrate,

$$C_6H_{18}\cdot CH[CH(CO_2Et)\cdot CO\cdot CO_2Et]_2,H_2O,$$

m. p. 115°, obtained from heptaldehyde (œnanthaldehyde) and ethyl oxalacetate, crystallises from dilute alcohol, and when heated at 110° decomposes without yielding the anhydrous ester. The *monophenylhydrazone*, m. p. 115—116°, crystallises from dilute alcohol, and the *monosemicarbazone*, m. p. 153°, crystallises from ether or from a mixture of this solvent with light petroleum. *Heptylidenebisoxalacetic dianhydride*, m. p. 89—90°, obtained by the action of cold sulphuric acid on the hydrated ester, is less stable than its lower homologues, furnishes a very unstable hydrate with cold water, and is decomposed by warm water, forming diketohexylpimelic acid, whilst alcohol and aniline furnish similarly the diethyl ester and the dianilide of the same acid respectively. Diketohexylpimelic acid is not produced when ethyl heptylidenebisoxalacetate hydrate is boiled with dilute mineral acids.

T. A. H.

The Action of Aluminium Alkyloxides on Aldehydes. Complex Ethereal Condensations considered as a New Form of Aldehyde Condensation. V. E. TISTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, ii, 355—418).—A historical survey of previous work on condensation is given. By the prolonged action of a small quantity of dry aluminium ethoxide on dry paraformaldehyde at the ordinary temperature, a mixture of ethyl and methyl formates are formed. Aluminium or magnesium methoxide with the same aldehyde yield chiefly methyl formate together with a little formic acid and possibly the compound $Mg[O\cdot CH(OMe)_2]_2$. Benzaldehyde behaves similarly, benzyl benzoate being the chief product; the main course of the reaction being $2CH_2O = H\cdot CO_2\cdot CH_3$; $2C_6H_5\cdot CHO = C_6H_5\cdot CO_2\cdot CH_2\cdot C_6H_5$. The following substances are formed by the interaction of aluminium ethoxide and acetaldehyde. Ethyl acetate, aldol, crotonaldehyde, ethyl alcohol, ethyl β-hydroxybutyrate and its acetyl derivative, mono- and diacetyl derivatives of βδ-dihydroxybutane, crotonic acid, and possibly also paraacetaldehyde and acetal. The main product is, however, ethyl acetate, but in the presence of water considerable quantities of aldol are also formed. As the amount of aluminium ethoxide employed is increased, the amount of aldehyde remaining unchanged diminishes, whilst the amount of ethyl acetate formed increases until the mixture contains 15% of ethoxide, after which any further addition of the latter diminishes the yield of ester. The temperature at which the experiment is performed exerts but little influence on the course of the reaction. About 80% of the ethoxide remains unchanged, the rest being converted into aluminium hydroxide, or, possibly, into more complex alkoxide compounds of aluminium.

Z. K.

Preparation of Aldehydes containing a Secondary Alkyl Group. GEORGES DARZENS (D.R.-P. 174239. Compare preceding abstract).—Aldehydes having the general formula $CHRR'\cdot CHO$ can be obtained from the ββ-substituted glycidic acids by heating these substances either alone or in the presence of water.

Methylnonylacetaldehyde, $C_9H_{19}\cdot CMe\cdot CHO$, b. p. 119—122°/10 mm., obtained by heating in a vacuum at 120° the glycidic acid produced from methyl nonyl ketone and ethyl chloroacetate, furnishes a semicarbazone, m. p. 101—102°.

p-Methylhydratropaldehyde, b. p. 107—108°/19 mm., was obtained by heating *p*-tolylmethylglycidic acid with water at 150°; it furnishes a semicarbazone, m. p. 159—160°. Ethyl benzylmethylglycidate when hydrolysed yields an acid which when heated at 140° in a vacuum gives rise to *β-phenyl-a-methylbutaldehyde*, $CH_2Ph\cdot CHMe\cdot CHO$, b. p. 129—130°/19 mm., it yields a semicarbazone, m. p. 70—72°. Many other aldehydes of this series have been prepared in a similar manner.

G. T. M.

Condensation Product of Ethoxyacetaldehyde with Acetaldehyde. Bruno Eissler and Alexander Pollak (*Monatsh.*, 1906, **27**, 1129—1144; Abstr., 1905, i, 683).—Ethoxyacetaldehyde condenses with acetaldehyde in presence of anhydrous potassium carbonate, forming *β-hydroxy-γ-ethoxybutaldehyde*,

$OEt{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$,

which is obtained as a yellow, viscid oil, b. p. 122—125°/18 mm., gives the aldehyde reactions, and when oxidised with alkaline potassium permanganate yields ethoxyacetic and oxalic acids. When heated with anhydrous sodium acetate at 120—130°, the aldol yields *γ-ethoxycrotonaldehyde*, $OEt{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CHO$, which forms a transparent liquid, b. p. 157°, and combines with 1 mol. of bromine. The aldol is oxidised by potassium permanganate in neutral solution, forming *β-hydroxy-γ-ethoxybutyric acid*, $OEt{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$, which is isolated in the form of its *calcium* salt, $(C_6H_{11}O_4)_2Ca$.

The *glycol*, $OEt{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 210°/760 mm., is prepared by reduction of the aldol with aluminium amalgam.

G. Y.

Fermentability of Methylglyoxal. Paul Mayer (*Biochem. Zeitsch.*, 1907, **2**, 435—437. Compare Büchner and Meisenheimer (*Ber.*, 1906, **39**, 3201).—Methylglyoxal in 1, 2, or 5% aqueous solution is not fermented by living yeast cells. J. J. S.

Unimolecular and Termolecular Glyoxal. Carl Harries and Paul Temme (*Ber.*, 1907, **40**, 165—172).—A unimolecular glyoxal, $CHO{\cdot}CHO$, is obtained when commercial glyoxal (Debus's polyglyoxal) is heated with phosphoric oxide, and the product collected in a vessel surrounded with a mixture of solid carbon dioxide and ether or with liquid air, care being taken to prevent the admission of atmospheric moisture. It forms golden yellow crystals, m. p. 15° and b. p. 51°/776 mm. or 50°/742 mm. Its vapour has an intense green colour, and condenses to a green liquid, which changes to yellow on cooling. The odour is similar to that of formaldehyde, and the vapour burns with a violet flame. Even at low temperatures it polymerises to an insoluble *paraglyoxal*, and in the presence of small amounts of water this change occurs instantaneously. The glyoxal dissolves in an excess of water, and the molecular weight determined by the cryoscopic method indicates that in such a solution the aldehyde is still unimolecular.

A termolecular glyoxal is obtained when cinnamaldehyde ozonide is warmed with water at 60—70°. It dissolves readily in water, and may be obtained from the aqueous solution by evaporating at 25—30° after the removal of benzaldehyde, benzoic acid, &c. If the temperature is raised above 30° a polymeric modification resembling the commercial product is obtained. The termolecular compound forms a yellow, amorphous mass insoluble in ether; it changes colour at 175° and decomposes at about 200°. Its aqueous solution is distinctly acid, and also reduces Fehling's solution. Its aqueous or alcoholic solutions yield derivatives of the unimolecular glyoxal; the *disemicarbazone*, $C_4H_8O_2N_6$, crystallises in rhombohedric prisms; the phenylosazone has

m. p. 167—168°; the diphenylosazone, 203°, and the phenylmethylosazone, 221°. The *tetraethyl acetal*, $CH(OEt)_2 \cdot CH(OEt)_2$, is a mobile liquid, b. p. 88—89°/14 mm., sparingly soluble in water. J. J. S.

Preparation of an Unsaturated Aldehyde from Formyl*iso*butacetaldol and an Attempt to Condense Formyl*iso*butacetaldol with Formaldehyde.

HANS BUSCH and KLARA GOLDENTHAL (*Monatsh.*, 1906, **27**, 1157—1166. Compare Weis, Abstr., 1905, i, 17; Schachner, *ibid.*, 171).—In one experiment the action of acetic anhydride and sodium acetate on formyl*iso*butacetaldol led to the formation of only a small amount of the unsaturated δ-acetoxyaldehyde, $OAc \cdot CH_2 \cdot CMe_2 \cdot CH:CH \cdot CHO$, which is obtained as a yellow oil, b. p. 83°/16 mm., reduces ammoniacal silver solutions, and forms an *additive* product with bromine, $C_9H_{14}O_3Br_2$. In another experiment two products were obtained; the *tetra-acetate*,

$$OAc \cdot CH_2 \cdot CMe_2 \cdot CH(OAc) \cdot CH_2 \cdot CH(OAc)_2,$$

which forms a colourless, mobile liquid, b. p. 83—90°/12 mm., and the *diacetate*, $OH \cdot CH_2 \cdot CMe_2 \cdot CH(OH) \cdot CH_2 \cdot CH(OAc)_2$, which is a slightly yellow, more viscid liquid, b. p. 137—138°/12 mm. When heated with potassium carbonate in an atmosphere of carbon dioxide in a reflux apparatus at 110—115°, the aldol yields the *acid*, $C_7H_{12}O_3$, which is obtained in yellow crystals, m. p. 104—105°, and forms an *additive* compound with bromine; the *calcium* salt, $(C_7H_{11}O_3)_2Ca$, forms white crystals. The corresponding unsaturated *aldehyde*, $C_7H_{12}O_2$, is prepared by heating the aldol with potassium carbonate in an atmosphere of carbon dioxide in a sealed tube at 110°; it crystallises in slender, yellow needles, m. p. 49—50°, sublimes at 65°/15 mm., gives the aldehyde reactions, forms an *additive* compound with bromine, and is oxidised on exposure to air yielding the preceding acid.

The condensation of the aldol with formaldehyde in potassium carbonate solution leads to the formation of ββ-dimethyltrimethylene glycol (Just, Abstr., 1896, i, 403). G. Y.

Preparation of the Corresponding Aldol from Ethoxyacetaldehyde.

WALTER FRIED (*Monatsh.*, 1906, **27**, 1251—1258. Compare Klüger, Abstr., 1905, i, 683; Eissler and Pollak, this vol., i, 183).—The action of potassium carbonate on ethoxyacetaldehyde and *iso*butaldehyde in concentrated aqueous solution leads to the formation of a mixture of aldols, b. p. 112—115°/18 mm.

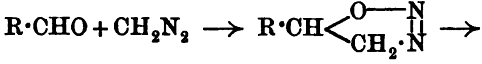
The *aldol* of ethoxyacetaldehyde [*β-hydroxy-αγ-diethoxybutaldehyde*], $OEt \cdot CH_2 \cdot CH(OH) \cdot CH(OEt) \cdot CHO$, prepared by the action of potassium carbonate on ethoxyacetaldehyde in concentrated aqueous solution cooled by ice, is obtained as a mobile, transparent liquid, b. p. 115—117°/18 mm., which gives the aldehyde reactions, and when heated with anhydrous sodium acetate in a current of carbon dioxide at 120—130° yields the *unsaturated aldehyde*,

$$OEt \cdot CH_2 \cdot CH:C(OEt) \cdot CHO,$$

b. p. 148° This reduces ammoniacal silver solutions, and forms in ethereal solution an *additive* compound with two atoms of bromine. G. Y.

Peroxide of Methyl Ethyl Ketone. Pastureau (*Compt. rend.*, 1907, **144**, 90—93).—*Methyl ethyl ketone peroxide*, $C_8H_{16}O_4$, obtained as a thick, colourless oil when methyl ethyl ketone is treated with hydrogen peroxide in the presence of sulphuric acid, has D^{15} 1·042. possesses an agreeable odour, is stable at the ordinary temperature, but very explosive when heated above 100°, and cannot therefore be distilled even under reduced pressure. When distilled with steam under reduced pressure, it yields a mixture of constant b. p. 48°/80 mm. or 56°/130 mm. It is completely reduced to methyl ethyl ketone by the action of nascent hydrogen in the cold; explodes violently when placed in contact with concentrated sulphuric acid, and is partially transformed into the original ketone and acetylmethylcarbinol by the action of dilute sulphuric acid. It yields the tetrabromo-derivative of methyl ethyl ketone, $CH_2Br\cdot CO\cdot CH_2\cdot CBr_3$, when treated with bromine. The acid mother liquor from which the peroxide is separated in the above preparation contains acetylmethylcarbinol, CHMeAc·OH, which yields the yellow osazone, m. p. 243°, and the blood-red osotetrazone (von Pechmann, Abstr., 1888, 1287). M. A. W.

Transformation of Aldehydes into Ketones by Means of Diazomethane. Fritz Schlotterbeck (*Ber.*, 1907, **40**, 479—483).—The author has studied the formation of ketones from aldehydes by means of diazomethane. Furodiazoles are probably formed as intermediate products, thus:



$$R\cdot CHO + CH_2N_2 \longrightarrow R\cdot CH<\begin{matrix}O\text{—}N\\ \| \\ CH_2\cdot N\end{matrix} \longrightarrow R\cdot CO\cdot CH_3 + N_2.$$

Methyl hexyl ketone was obtained from heptaldehyde, acetophenone from benzaldehyde, and methyl *iso*butyl ketone from *iso*valeraldehyde, the ketones having been identified in each case by means of their semicarbazones. A. McK.

New Synthesis of α-Diketones. Leo Tschugaeff (*Ber.*, 1907, **40**, 186—187).—Diacetyl and dipropionyl are formed by the action of magnesium methyl and magnesium ethyl bromides respectively on vinylideneoxanilide (von Pechmann, Abstr., 1898, i, 135).

Nickel diethylglyoxime, $Ni(NO\colon CEt\cdot CEt\colon N\cdot OH)_2$, has also been prepared, and crystallises in orange-red needles. G. Y.

Solubility of Sucrose in Water in Presence of Invert-sugar. Henri Pellet and Ch. Fribourg (*Chem. Centr.*, 1906, ii, 1722; from *Bull. Assoc. Chim. Sucr. Dist.*, **24**, 304—315).—Experiments have shown that a saturated solution of sucrose can dissolve invert-sugar and that a saturated solution of crystalline sucrose can after inversion dissolve sucrose. In a saturated solution containing equal weights of sucrose and invert-sugar, 1 part of water holds 3·5 of dry substances in solution at 29°, whilst under similar conditions in a solution of pure sucrose, 2·18—2·22 are dissolved by 1 part of water. A solution of invert-sugar saturated with sucrose at 29° contains 69 parts of sucrose per 100 of invert-sugar, and 3·9 of dry substances are dissolved by 1 part of water.

The viscosity of a saturated solution of sucrose increases in proportion to the quantity of invert-sugar contained in it. E. W. W.

Cellulose. Hermann Wichelhaus and Walther Vieweg (*Ber.*, 1907, 40, 441—443).—The view that in mercerising cellulose only the cuticle of the fibre is removed (compare Fränkel and Friedlander, *Mitt. K. K. Techn. Gewerbemus., Wien*, 1898, 326) is incorrect. By comparing the esters of nitric and benzoic acids derived from the natural and mercerised cellulose the change is shown to be chemical in character. The yield of benzoate, obtained from 100 parts of cellulose by the action of benzoyl chloride and sodium hydroxide, is:

	Before.	After mercerising.
Cotton wool	112	139
Flax	121	137

Again, although the % of nitrogen in the nitrates derived from cotton, cotton wool, or flax both before and after treatment is practically constant (13%), the products are chemically different, as the portion soluble in a mixture of alcohol and ether is increased by mercerisation. W. R.

Constituents of Lignocelluloses which Yield Furfuraldehyde and Methylfurfuraldehyde. Konrad Fromherz (*Zeitsch. physiol. Chem.*, 1906, 50, 209—240).—Lignocellulose has been prepared from the wood of the aspen (*Populus tremula*) by Lange's method, the yield being 55%. Certain of the constituents which yield furfuraldehyde and methylfurfuraldehyde are dissolved when heated with water under pressure at 150°. These constituents probably resemble the "furoids" obtained by Cross and Bevan from straw. The mannans and galactans are also dissolved during this process. Dextrose could not be detected, and lævulose was present in small quantities only.

Part of the furfuraldehyde is derived from the cellulose of the wood, and is formed mainly from oxidised groups. The cellulose also yields methylfurfuraldehyde, whereas cellulose from filter paper, when heated with water under pressure, yields only the minutest traces of this aldehyde.

The yields of furfuraldehyde from lignocellulose or cellulose and the yield of methylfurfuraldehyde from rhamnose decrease with the process of heating, whereas the yields of methylfurfuraldehyde from the lignocellulose and cellulose of the wood increase, up to a certain point, on heating with water. J. J. S.

Some Reactions of Sodamide. Louis Meunier and E. Desparmet (*Compt. rend.*, 1907, 144, 273—275).—The action of sodamide on polyhaloid derivatives of the hydrocarbons is very similar to that of alcoholic potash. With ethylene dibromide, it gives acetylene. With chloroform, the reaction is slower in commencing, but becomes explosive, bromoform reacts similarly and even more violently; if, however, powdered sodamide is added in small quantities to excess of chloroform and the latter warmed slightly, ammonia is evolved and a mixture of sodium chloride and cyanide precipitated. This reaction can be expressed by an equation $CHCl_3 + 4NaNH_2 = NaCN + 3NaCl + 3NH_3$, precisely similar to that for the preparation of the carbylamines. Moreover, chloroform diluted with anhydrous benzene, when heated with aniline (1 mol.) and sodamide (3 mols.), gives phenylcarbylamine, thus: $NH_2Ph + CHCl_3 + 3NaNH_2 = 3NaCl + 3NH_3 + PhNC$.

Sodamide can be employed for the preparation of sodium derivatives (compare Alexéeff, *Journ. Russ. Phys. Chim. Soc.*, 1902, **34**, 526; Titherley, *Proc.*, 1902, **18**, 186; Haller, Abstr., 1905, i, 214; and Claisen and Feyerabend, Abstr., 1905, i, 286). Aniline, diphenylamine, and diazoaminobenzene readily give sodium derivatives. Addition of diphenylamine in ethereal solution to benzyl chloride in the same solvent containing a slight excess of sodamide causes a vigorous reaction with evolution of ammonia and formation of diphenylbenzylamine.

Ethyl malonate, when treated in cold benzene solution with sodamide, forms a transparent jelly probably consisting of the additive compound, $NH_2\cdot C(OEt)(ONa)\cdot CH_2\cdot CO_2Et$, which, when heated, evolves ammonia and gives the sodium derivative,

$$CHNa(CO_2Et)_2.$$

When anhydrous acetaldehyde is added to sodamide covered with dry ether, a white, crystalline precipitate, stable in dry air, is formed, whilst ammonia is evolved and combines with the aldehyde, forming aldehyde-ammonia. The evolution of ammonia can only be explained by the dehydration of the aldehyde and formation of the sodium derivative of the corresponding imine, $CH_3\cdot CHO + 2NaNH_2 = CH_3\cdot CH\colon NNa + NaOH + NH_3$. The crystalline precipitate is therefore probably a mixture of aldehyde-ammonia and the sodimino-derivative. This explanation agrees with Delépine's work on aldehyde-ammonia (Abstr., 1898, i, 462). E. H.

Relative Stability of some Metalammine Compounds. LEO TSCHUGAEFF (*Ber.*, 1907, **40**, 173—181. Compare Abstr., 1904, i, 478; 1905, i, 865; 1906, i, 814).—The capacity of a number of primary, secondary, and tertiary amines to form complex compounds with copper, silver, platinum, and nickel salts in *N*/10 solution has been investigated qualitatively and found to diminish as the number of *N*-hydrogen atoms substituted is increased.

On addition of methyl-, ethyl-, *n*-propyl-, *iso*propyl-, *n*-butyl-, *iso*butyl-, *tert.*-butyl-, *sec.*-butyl-, *n*-amyl-, *iso*amyl-, *tert.*-amyl-, or vinyl-amine to aqueous copper chloride, copper hydroxide is precipitated and dissolves on addition of an excess of the amine, forming the characteristic blue solution; with camphylamine, fenchylamine, or thujylamine the addition of alcohol is necessary for complete solution of the blue compound, which may be extracted with ether, chloroform, or benzene. The red compounds, $(Su)_2Cu,2a$, [$Su = C_2H_4(CO)_2N$; a = an amine], is formed on addition of succinimide to the blue solutions.

Under the same conditions, secondary amines such as diethyl-, di-*n*-propyl-, di-*iso*butyl-, di-*iso*amyl-, and dibenzyl-amine dissolve only small quantities of the precipitated copper hydroxide, whilst this is completely insoluble in tertiary amines: trimethyl-, triethyl-, tri-*n*-propyl-, tri*iso*butyl-, and tri*iso*amyl-amines, which do not form complex metallic compounds in either aqueous or alcoholic solution. On prolonged contact with trimethylamine, copper hydroxide is converted into the black oxide.

The aliphatic amines react in the same manner with dilute silver nitrate, forming a black precipitate of silver oxide which is dissolved by an excess of the primary amines. Camphylamine forms with silver oxide a crystalline *compound* which is soluble in alcohol.

The primary aliphatic amines form complex compounds with silver succinimide with development of heat (compare Landsberg, Abstr., 1883, 476). *Benzylamine silver succinimide*, $(Su)Ag,CH_2Ph{\cdot}NH_2$, crystallises from alcohol in nacreous leaflets, and commences to become brown in a sealed capillary tube at 160°, m. p. about 190° (decomp.).

Silver oxide precipitated by addition of secondary or tertiary amines to dilute silver nitrate is dissolved by an excess of the secondary amines to a less extent than is copper hydroxide, whilst it is almost insoluble in excess of the tertiary amines in which even silver chloride is barely soluble.

The behaviour of silver salts with pyridine and quinoline bases is completely analogous with that of the copper salts (Jörgensen, Abstr., 1886, 857).

Whilst the action of primary aliphatic amines on potassium platinichloride in aqueous solution leads to the formation of platoso-diamine chlorides and platoso-diamine platinosochlorides (Jörgensen, *loc. cit.*), tertiary amines precipitate metallic platinum slowly at the ordinary temperature or quickly on boiling, trimethylamine yielding an odour of acetaldehyde.

With nickel salts and aliphatic amines there have been obtained in addition to the succinimide compounds derived from primary amines, $(Su)_2Ni,2a$ (Abstr., 1906, i, 814), only an unstable *derivative* of dimethylamine.

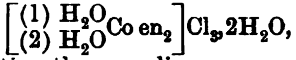
[With J. SURENJANZ.]—Tetramethylethylenediamine does not form complex compounds with nickel salts (compare Werner, Abstr., 1899, i, 856; Kurnakoff, Abstr., 1900, i, 209).

The difference of the behaviour of the pyridine bases from that of the aliphatic secondary amines is discussed and considered to support Euler's views on the formation of complex ions (Abstr., 1904, ii, 379).

G. Y.

Stereoisomeric Diaquodiethylenediaminecobalt Salts. ALFRED WERNER [and, in part, G. JANTSCH] (*Ber.*, 1907, 40, 262—271).—The salts of this series are obtained initially from complex ethylenediaminecobalt compounds, which are formed by atmospheric oxidation of aqueous cobalt nitrate or sulphate in the presence of ethylenediamine, and which will be described in a future paper.

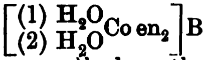
cis-*Diaquodiethylenediaminecobalt chloride*,



$$\left[\begin{matrix}(1)\ H_2O \\ (2)\ H_2O\end{matrix}\mathrm{Co\,en_2}\right]Cl_3,2H_2O,$$

is obtained by triturating the preceding compounds with hydrochloric acid, saturated at 0°, or from *hydroxoaquodiethylenediaminecobalt* *bromide* in a similar manner. ("Hydroxo" indicates the hydroxyl group in direct union with the metallic atom.) This basic bromide, $\left[\begin{matrix}HO\\H_2O\end{matrix}Co\,en_2\right]Br_2,H_2O$, is precipitated in red crystals by the addition of pyridine and powdered potassium bromide to the syrup obtained by the evaporation of an aqueous solution of dinitratodiethylenediaminecobalt nitrate (*A. Lieben. Festschrift*, 211).

cis-*Diaquodiethylenediaminecobalt bromide*,

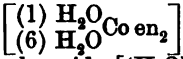


$$\left[\begin{matrix}(1)\ H_2O\\(2)\ H_2O\end{matrix}Co\,en_2\right]Br_3,2H_2O,$$

is obtained by the same methods as the chloride. The two salts form red crystals and are extremely soluble in water, forming solutions with an acid reaction. At 115° the salts lose $4H_2O$, the chloride forming *cis*-dichlorodiethylenediaminecobalt chloride (violeochloride) and a small quantity of the green *trans*-isomeride, whereas the bromide yields chiefly *trans*-dibromodiethylenediaminecobalt bromide (praseobromide). The *cis*-diaquo-chloride or bromide in boiling aqueous solution is converted by hydrochloric or hydrobromic acid into *trans*-dichlorodiethylenediaminecobalt chloride or the corresponding bromide, whilst potassium hydroxide converts them into *cis*-hydroxoaquodiethylenediaminecobalt chloride (or bromide).

The configuration of the two salts is ascertained by treating them with sodium nitrite and acetic acid, whereby an unstable dinitritodiethylenediaminecobalt salt, $[(ON\cdot O)_2Co\,en_2]X$, is obtained, which changes into 1 : 2-dinitrodiethylenediaminecobalt nitrite.

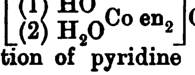
trans-*Diaquodiethylenediaminecobalt chloride*,



$$\left[\begin{matrix}(1)\ H_2O\\(6)\ H_2O\end{matrix}Co\,en_2\right]Cl_3,2H_2O,$$

and the corresponding *bromide*, $[(H_2O)_2Co\,en_2]Br_3,2H_2O$, are obtained by treating 1 : 6-hydroxoaquodiethylenediaminecobalt bromide (compare following abstract) with the concentrated halogen acid, or from Werner and Bräunlich's di-*iso*thiocyanodiethylenediaminecobalt thiocyanate (Abstr., 1900, i, 86) in the following way. An aqueous solution of the thiocyanate is heated with potassium hydroxide, cooled, and treated with hydrobromic acid; the reddish-brown precipitate of 1 : 6-hydroxoaquodiethylenediaminecobalt thiocyanate is dissolved in 50% acetic acid and treated with sodium nitrite, whereby 1 : 6-dinitritodiethylenediaminecobalt thiocyanate is obtained, which by trituration with concentrated hydrochloric or hydrobromic acid yields the required salt. The *trans*-diaquo-chloride forms glistening, reddish-brown needles, the bromide violet-brown leaflets. Both contain $2H_2O$, which is lost readily. By stronger heating, the chloride is converted mainly into the dichlorovioleo-chloride, whilst the bromide yields only the dibromopraseo-bromide. C. S.

Theory of Hydrolysis and Stereoisomeric Hydroxoaquodiethylenediaminecobalt Salts. ALFRED WERNER (*Ber.*, 1907, 40, 272—287).—cis-*Hydroxoaquodiethylenediaminecobalt chloride*,



$$\left[\begin{matrix}(1)\ HO\\(2)\ H_2O\end{matrix}Co\,en_2\right]Cl_2,H_2O,$$

obtained by the addition of pyridine or, less suitably, of potassium hydroxide to an aqueous solution of *cis*-diaquodiethylenediaminecobalt chloride, is a brownish-red, crystalline powder, and is reconverted into the diaquochloride by concentrated hydrochloric acid. From an aqueous solution of the substance which has been heated at 115° before solution, triethylenediaminecobalt salts and ethylenediaminecobalt salts can be obtained.

cis-*Hydroxoaquodiethylenediaminecobalt bromide*,

$$\left[\begin{matrix}\mathrm{HO}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Br_2,H_2O},$$

is obtained (1) like the preceding compound; (2) by treating *trans*-dichlorodiethylenediaminecobalt chloride (praseo-chloride) with concentrated potassium hydroxide and neutralising the resulting solution with cold concentrated hydrobromic acid; (3) in a similar manner from *cis*-dichlorodiethylenediaminecobalt chloride (violeo-chloride). It forms a red, crystalline powder and possesses properties similar to those of the chloride.

The *iodide*, $\left[\begin{matrix}(1)\ \mathrm{HO}\\ (2)\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{I_2,H_2O}$, is obtained in small, brownish-red needles by treating an aqueous solution of *cis*-diaquodiethylenediaminecobalt bromide with pyridine and powdered potassium iodide.

The *dithionate*, $\left[\begin{matrix}(1)\ \mathrm{HO}\\ (2)\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{S_2O_6}$, crystallises in slender, violet-red needles, and is prepared by adding pyridine and saturated sodium dithionate to the solution of the syrup obtained by the evaporation, after prolonged boiling, of an aqueous solution of dinitratodiethylenediaminecobalt nitrate.

trans-*Hydroxoaquodiethylenediaminecobalt chloride*,

$$\left[\begin{matrix}(1)\ \mathrm{HO}\\ (6)\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Cl_2},$$

is obtained from aqueous *trans*-diaquodiethylenediaminecobalt chloride in pearly-bluish-red leaflets by the addition of potassium hydroxide, or, less readily, in needles by the addition of pyridine.

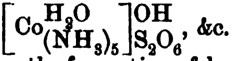
The *bromide*, $\left[\begin{matrix}(1)\ \mathrm{HO}\\ (6)\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{Br_2}$, is obtained similarly, or better, by boiling an aqueous solution of the *cis*-compound for two minutes with potassium hydroxide and neutralising the well-cooled solution with hydrobromic acid. It is a light red, crystalline powder; the cryoscopic method in aqueous solution indicates the presence of three ions, $\left[\begin{matrix}\mathrm{HO}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]$ and 2Br.

The *iodide*, $\left[\begin{matrix}(1)\ \mathrm{HO}\\ (6)\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{I_2}$, is obtained in pearly reddish-brown leaflets by decomposing an aqueous solution of *trans*-diaquodiethylenediaminecobalt chloride with concentrated potassium hydroxide followed by the addition of potassium iodide.

The *dithionate*, $\left[\begin{matrix}(1)\ \mathrm{HO}\\ (6)\ \mathrm{H_2O}\end{matrix}\mathrm{Co\,en_2}\right]\mathrm{S_2O_6}$, obtained by the addition of saturated sodium dithionate to an aqueous solution of *trans*-hydroxoaquodiethylenediaminecobalt chloride, crystallises in glistening, red needles.

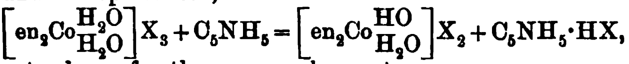
The salts of the *cis*- and *trans*-hydroxoaquodiethylenediaminecobalt series have a faintly alkaline reaction, but do not precipitate silver oxide from silver nitrate solution or absorb carbon dioxide; mineral acids convert them into salts of the diaquo-series. They are, as a rule, sparingly soluble in water, but dissolve readily in the presence of acetic acid, forming solutions from which metallic salts precipitate the corresponding hydroxoaquo-salt.

The properties of these salts of the basic diethylenediaminecobalt series, those of Pfeiffer's pyridine chromium compounds (Abstr., 1906, i, 531), and those even of Jörgensen's pentammine and tetrammine cobalt and chromium salts (Abstr., 1883, 554; 1891, 1325; 1898, ii, 226) cannot be rationally interpreted by Jörgensen's theory that the hydroxyl group is linked to a water molecule, thus:



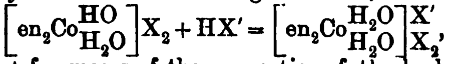
$$\left[\mathrm{Co}\begin{matrix}H_2O\\(NH_3)_5\end{matrix}\right]\begin{matrix}OH\\S_2O_6\end{matrix},\ \&c.$$

By the author's theory the formation of hydroxoaquo- from diaquo-compounds is represented,



$$\left[\mathrm{en_2Co}\begin{matrix}H_2O\\H_2O\end{matrix}\right]X_3+C_5NH_5=\left[\mathrm{en_2Co}\begin{matrix}HO\\H_2O\end{matrix}\right]X_2+C_5NH_5\cdot HX,$$

and the tendency for the reverse change to occur,

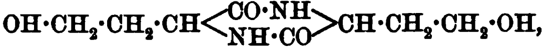


$$\left[\mathrm{en_2Co}\begin{matrix}HO\\H_2O\end{matrix}\right]X_2+HX'=\left[\mathrm{en_2Co}\begin{matrix}H_2O\\H_2O\end{matrix}\right]\begin{matrix}X'\\X_2\end{matrix},$$

serves to account for many of the properties of the hydroxoaquo-salts. An attempt is made to explain the formation and reactions of hydroxo-salts by the aid of the ionic hypothesis. C. S.

Synthesis of α-Amino-γ-hydroxybutyric Acid. EMIL FISCHER and HERBERT BLUMENTHAL (*Ber.*, 1907, **40**, 106—113).—*α-Bromo-γ-phenoxyethylmalonic acid*, $OPh\cdot CH_2\cdot CH_2\cdot CBr(CO_2H)_2$, obtained by the gradual addition of bromine to an ethereal solution of γ-phenoxyethylmalonic acid (prepared according to Perkin, Bentley, and Haworth, Trans., 1896, **69**, 165) separates from benzene in rhombic crystals, m. p. 148° (corr.) with evolution of gas. When heated at 150—155° it evolves carbon dioxide and is converted into *α-bromo-γ-phenoxybutyric acid*, $OPh\cdot CH_2\cdot CH_2\cdot CHBr\cdot CO_2H$, which separates from a mixture of ether and light petroleum in stellate prisms and has m.p. 101·5° (corr.).

α-Amino-γ-phenoxybutyric acid, $OPh\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, obtained by agitating the preceding compound with aqueous ammonia and then either allowing the mixture to remain at the ordinary temperature for four to five days or heating in a closed vessel for three hours at 100°, separates from water in colourless needles, m. p. 233° (decomp.). When boiled with strong hydrobromic acid, phenol and α-amino-γ-hydroxybutyric acid, $OH\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, are formed, the latter readily passing into its lactone which crystallises out in the form of its hydrobromide. *α-Aminobutyrolactone hydrobromide*, $C_4H_8O_2NBr$, separates from alcohol in glistening, almost colourless pyramids, m. p. 227° (corr.) (decomp.); when treated with silver carbonate, it forms either the lactone or the free acid according to the conditions. *α-Amino-γ-hydroxybutyric acid*, $OH\cdot CH_2\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, crystallises from aqueous alcohol in silky, colourless needles, m. p. 187° (corr.) (decomp.), it has a very faint acid reaction towards litmus. Its *copper* salt forms dark blue prisms. Its *hydrochloride*, $C_4H_8O_2NCl,H_2O$, separates from aqueous alcohol in prisms; when dehydrated, it has m. p. 201—203° (corr.) (decomp.).

α-Aminobutyrolactone may be obtained in the crude form as an oil by the addition of potassium carbonate to an aqueous solution of α-aminobutyrolactone hydrobromide; on exposure at the ordinary temperature it solidifies, being converted into *di-β-hydroxyethyldiketopiperazine*,  $OH\cdot CH_2\cdot CH_2\cdot CH<\begin{smallmatrix}CO\cdot NH\\ NH\cdot CO\end{smallmatrix}>CH\cdot CH_2\cdot CH_2\cdot OH$, which crystallises from alcohol; it softens at 185° and has m. p. 192° (corr.). In aqueous solution it is neutral and does not form a copper salt. The substance is possibly a mixture of two stereoisomerides.

α-Benzoylamino-γ-hydroxybutyric acid, $OH\cdot CH_2\cdot CH_2\cdot CH(NHBz)\cdot CO_2H$, prepared by the addition of benzoyl chloride and sodium hydroxide to α-aminobutyrolactone hydrobromide, separates from water in colourless needles, which soften at 117° and have m. p. 121° (corr.). Its aqueous solution gives an acid reaction, and when boiled for several minutes is converted into *α-benzoylaminobutyrolactone*, $C_{11}H_{11}O_3N$, which separates in hard crystals; it softens at 137° and has m. p. 142° (corr.).

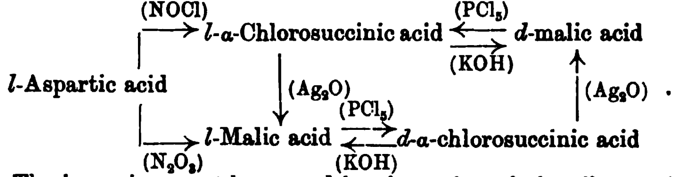
A. McK.

Action of Acid Anhydrides on Creatine and on Creatinine. F. Urano (*Beitr. chem. Physiol. Path.*, 1907, 9, 183—184. Compare Erlenmeyer, junr., Abstr., 1895, i, 310).—*Benzoylcreatinine*, $C_{11}H_{11}O_2N_3$, is formed when benzoic anhydride is heated with creatine at 120° or with creatinine at 150°. It crystallises from 95% alcohol in pale yellow needles, m. p. 187°.

Phthalyldicreatine, $C_6H_4[CO\cdot NH\cdot C(NH)\cdot NMe\cdot CH_2\cdot CO_2H]_2$, obtained by heating phthalic anhydride with creatine or creatinine at 140° for ten hours, crystallises from alcohol in slender, colourless needles, m. p. 212°.

J. J. S.

Walden's Inversion. Emil Fischer (*Ber.*, 1907, 40, 489—508. Compare Walden, Abstr., 1896, i, 205; 1898, i, 127, 178; 1899, ii, 538).—The results of Walden's experiments on the change of an active substance into its antipode without the intermediate formation of the racemic form can be formulated by the scheme:



The inversion must be caused by the action of the silver oxide or of the potassium hydroxide (or phosphorus pentachloride); Walde regards the latter as producing an optically normal reaction, that is one without change of configuration. If this be so, either nitrosyl chloride or nitrous acid must cause inversion by its action on *l*-aspartic acid.

Similar inversions have been performed by the author with alanine

(Abstr., 1905, i, 692), leucine (Abstr., 1906, i, 808), and phenylalanine :

$$\begin{tikzcd}
 & l\text{-Bromopropionic acid} \arrow[dr, "(NH_3)"] & \\
d\text{-Alanine} \arrow[ur, "(NOBr)"] & & l\text{-Alanine} \arrow[dl, "(NOBr)"] \\
 & d\text{-Bromopropionic acid} \arrow[ul, "(NH_3)"] &
\end{tikzcd}$$

The active *a*-bromopropionic acid or its ester is converted into the amino-acid of the same sign by aqueous or liquid ammonia or by potassium phthalimide, whereas by the action of nitrosyl bromide, *d*-alanine and its ester yield bromopropionic acid and ester of opposite signs.

d-Alanine ⟶ *l*-bromopropionic acid
d-Alanine ester ⟶ *d*-bromopropionic ester.

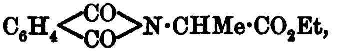
This result, which has been observed in the case of other amino-acids, indicates that optical inversion is caused by the action of nitrosyl chloride or bromide.

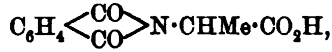
Walden's contention that potassium hydroxide or phosphorus pentachloride causes an optically normal reaction is supported by his own observation that active haloid acids and their esters are changed into hydroxy-acids and esters of the same sign by the former, whereas *d*-lactic acid or its ester yields *d*-chloropropionic acid by the action of the latter. Moreover, aqueous *d*-chloropropionic acid is converted by silver oxide into *l*-lactic acid (Purdie and Williamson, Trans., 1896, **69**, 837), whilst natural *d*-alanine yields *d*-lactic acid by the action of nitrous acid (Fisher and Skita, Abstr., 1901, i, 783). The author confirms these results by showing that *l*-bromopropionic acid is converted into *d*-lactic acid by silver oxide or carbonate and into *l*-lactic acid by dilute potassium hydroxide.

The ester of *l*-bromopropionic acid does not react with silver oxide at low temperatures ; *l*-bromopropionylglycine, however, yields a substance which is hydrolysed to *l*-lactic acid. The action of silver oxide on an haloid acid and its esters is similar to that of nitrosyl bromide on active hydroxy-acids and their esters.

Little can be said at present concerning the mechanism whereby optical inversion is produced. Walden regards the abnormal reactions caused by silver or mercuric oxide as due to the formation of unstable additive products by the decomposition of which a change of configuration is rendered possible. Evidence of the formation of additive compounds has been obtained by the author in a few cases which are described below.

The new compounds recorded are :

Ethyl l-*a-phthalylalanine*,  $C_6H_4<\substack{CO\\CO}>N\cdot CHMe\cdot CO_2Et$, containing about 42% of the racemic form, is obtained by heating ethyl *l*-*a*-bromopropionate and powdered potassium phthalimide for five hours at 125° to prevent racemisation as much as possible (compare Gabriel and Colman, Abstr., 1900, i, 358) ; it has m. p. 58—60° and $[a]_D^{20}$ 7·15° in alcoholic solution.



Phthalyl-d-*alanine*, $C_6H_4<\substack{CO\\CO}>N\cdot CHMe\cdot CO_2H$, m. p. 150—151° (corr.) softening at 139°, is obtained by heating *d*-alanine and phthalic anhydride for seven hours at 120—125°; it separates from hot water in small, quadrangular leaflets, has $[\alpha]_D^{20}$ − 17·84° in alcoholic solution, and yields *d*-alanine by hydrolysis with 20% hydrochloric acid; the *ethyl* ester has m. p. 54—56° (corr.) and $[\alpha]_D^{20}$ − 12·46°.

By the action of excess of bromine on ethyl *d*-alanine or ethyl *l*-leucine in a minimal quantity of 20% hydrobromic acid, in a freezing mixture, red oils are obtained, which seem to consist of additive compounds of bromine and the ester; they are decomposed by nitric oxide, yielding respectively ethyl *d*-α-bromopropionate and ethyl *d*-α-bromo*iso*hexoate.

Ethyl l-*α-bromo*iso*hexoate*, prepared from *l*-α-bromo*iso*hexoic acid, obtained from *l*-leucine and nitrosyl bromide, has b. p. 49—54°/0·5 mm., $[\alpha]_D^{20}$ − 43·1°, and contains some of the racemic form.

l-*α-Bromopropionylglycine*, $CHMeBr\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 120° (corr.), is obtained conveniently from glycine and *l*-α-bromopropionyl chloride; it crystallises in large prisms, $[\alpha]_D^{20}$ − 35·27° in aqueous and − 46·6° in alcoholic solution. By treatment with water and silver carbonate it yields at first slender needles of a silver salt, but after long keeping and evaporation a viscous liquid is obtained, probably consisting of the active lactylglycine, which by hydrolysis yields *l*-lactic acid.

r-*Lactylglycine*, $OH\cdot CHMe\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, prepared from *r*-α-bromopropionylglycine in a similar manner, has m. p. 108·5—109·5° (corr.). C. S.

Aminolactaldehyde. ALFRED WOHL and H. SCHWEITZER (*Ber.*, 1907, **40**, 92—102).—*α-Chloro-β-hydroxypropaldehyde methyl acetal*, $OH\cdot CH_2\cdot CHCl\cdot CH(OMe)_2$, best obtained by preparing the requisite hypochlorous acid by passing a current of chlorine into an aqueous solution of sodium hydrogen carbonate and then adding acraldehyde dimethyl acetal (compare Abstr., 1898, i, 555), has b. p. 97—98°/11 mm. Its *benzoyl* derivative has b. p. 68°/0·25 mm.

α-Chloro-β-benzoylhydroxypropaldehyde ethyl acetal,

$$OBz\cdot CH_2\cdot CHCl\cdot CH(OEt)_2,$$

has b. p. 128°/0·3 mm.

The constitution of α-chloro-β-hydroxypropaldehyde methyl acetal is indicated by its behaviour on oxidation with alkaline potassium permanganate, when the potassium salt of the acid,

$$CO_2H\cdot CHCl\cdot CH(OMe)_2,$$

is formed. By the action of methyl iodide, the latter salt was converted into the *methyl ester*, $CO_2Me\cdot CHCl\cdot CH(OMe)_2$, b. p. 86°/11 mm. The corresponding *ethyl ester*, $CO_2Et\cdot CHCl\cdot CH(OEt)_2$, has b. p. 116—117°/11 mm.

Aminolactaldehyde methyl acetal, $NH_2\cdot CH_2\cdot CH(OH)\cdot CH(OMe)_2$, obtained by heating a mixture of α-chloro-β-hydroxylpropaldehyde methyl acetal and sodium iodide with methyl alcoholic ammonia at 120° for forty-eight hours, has b. p. 100—111°/11 mm. and separates from ethyl acetate in needles, m. p. 55—58°.

Aminolactaldehyde ethyl acetal, $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH(OEt)_2$, has b. p. 120—121°/14 mm.

Aminolactaldehyde hydrochloride, $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CHO,HCl$, obtained by the action of fuming hydrochloric acid on aminolactaldehyde methyl acetal, crystallises in needles and begins to decompose at 137°. It reduces both Fehling's solution and ammoniacal silver nitrate. Its *semicarbazone*, $CH_2(NH_3Cl) \cdot CH(OH) \cdot CH{:}N \cdot NH \cdot CO \cdot NH_2,2MeOH$, is hygroscopic, softens at 72°, and has m. p. 74—75°. Its *platinichloride* begins to decompose at 155°.

When aminolactaldehyde hydrochloride is oxidised by bromine it forms *iso*serine.

When aminolactaldehyde hydrochloride is dissolved in ethyl alcohol and a few drops of chloroform are added and the mixture agitated for twenty-four hours at the ordinary temperature with diethylamine, *anhydrobisaminolactaldehyde* (iso*serine aldehyde*),

$$[NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH{:}N \cdot CH_2 \cdot CH(OH) \cdot CHO]_3,$$

is obtained as a white powder. The aqueous solution of the latter compound gives an alkaline reaction; it reduces ammoniacal silver nitrate and boiling Fehling's solution, and begins to decompose at 125°. When its molecular weight is determined by the cryoscopic method in aqueous solution, values are obtained for a termolecular compound; after standing two days, the values indicate a bimolecular structure and finally, after five days, a unimolecular structure. Dilute hydrochloric acid converts the anhydro-compound, either in its unimolecular or in its termolecular form, at the ordinary temperature into the aminoaldehyde hydrochloride. A. McK.

Constitution of Cyanic Acid. F. CARLO PALAZZO and EDUARDO CARAPELLE (*Chem. Centr.*, 1906, ii, 1723—1724; from *Estr. Giorn. Sci. Nat. Econ.*, 26. Compare Nef, Abstr., 1896, i, 71).—Since the action of diazomethane (compare Meyer, Abstr., 1906, i, 108) on cyanic acid yields a derivative of a carbamide, the author concludes that free cyanic acid is not tautomeric, but has the formula $O{:}C{:}NH$, and that its salts are also carbimides. The action of the acid on diazomethane is somewhat energetic. When the ethereal solution of the acid at −12° is poured into the ethereal solution of diazomethane at −5° and the mixture treated with dry ammonia, methylcarbamide, $NH_2 \cdot CO \cdot NHMe$, m. p. 101—102°, is the main product. Diazoethane yields ethylcarbamide; methyl ethylcarbamate, $NHEt \cdot CO_2Me$, b. p. 96—100°/50 mm., 70—73°/19 mm. (compare Klobbie, *Rec. trav. chim.*, 1888, 7, 355), is also formed from the methyl alcohol which always accompanies diazoethane (compare von Pechmann, Abstr., 1899, i, 134). E. W. W.

Preparation of Cyanoacetylcarbamide and its Alkyl and Amyl Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 175415).—It has been found that cyanoacetylcarbamide and its derivatives can be readily obtained by condensing cyanoacetic acid and carbamide or one of its alkyl or acyl derivatives with an acid anhydride. A mixture of carbamide, cyanoacetic acid, and acetic anhydride when warmed on the water-bath furnishes pure cyanoacetylcarbamide. Methylcarbamide, cyanoacetic acid, and propionic anhydride give cyanoacetylmethylcarbamide. Dimethylcarbamide, cyanoacetic acid, and acetic anhydride yield cyanoacetyldimethylcarbamide, whilst phenylcarbamide, cyanoacetic acid, and benzoic anhydride give rise to *cyanoacetylphenylcarbamide* (m. p. 216°).

G. T. M.

New Synthesis of Fulminic Acid. The Formation of Fulminic Acid from Alcohol and Nitric Acid. Heinrich Wieland (*Ber.*, 1907, **40**, 418—422).—When methylnitrolic acid is boiled for a short time with dilute nitric acid and silver or mercuric nitrates, the corresponding salt of fulminic acid crystallises out; the by-products of the interaction are formic acid, nitrous oxide, carbon dioxide, ammonia, and a small quantity of nitrous acid and nitric oxide.

The interaction of nitric acid and alcohol is explained by the following scheme:

$$CH_3\cdot CH_2\cdot OH \longrightarrow CH_3\cdot CHO \longrightarrow CH(:NOH)\cdot CO_2H \longrightarrow$$
$$NO_2\cdot C(:NOH)\cdot CO_2H \longrightarrow NO_2\cdot C(:NOH)H \longrightarrow HNO_2 + C:NOH.$$

The experimental support for the above hypothesis is as follows. Wöhler (Abstr., 1905, i, 418) found aldehyde a more suitable agent than alcohol for the preparation, whilst the formation of methylnitrolic acid from *iso*nitrosoacetic acid has been accomplished by Ponzio (Abstr., 1903, i, 453).

W. R.

Iron-Cyanogen Compounds. IV. Karl A. Hofmann [with H. Arnoldi and H. Hiendlmaier] (*Annalen*, 1907, **352**, 54—72).—With the object of showing the truth of the former statement (Abstr., 1906, i, 75) that the blue iron-cyanogen compounds, formed either from ferric salts and ferrocyanide or ferrous salts and ferricyanides, are derivatives of potassium ferrocyanide in which potassium is either wholly or partly replaced by tervalent iron, the reduction of mixed solutions of ferric salts and potassium ferricyanide has been studied. It has been further shown that those compounds, believed by several investigators to be ferrous cyanide, are really complex iron-cyanogen compounds. The *compound* $Fe_2C_6N_6H,2\frac{1}{2}H_2O$ is obtained by treating a solution containing molecular proportions of potassium ferricyanide and ferric alum with hydrogen peroxide; since this compound differs only from that obtained by treating soluble Prussian blue with dilute acid in the percentage of water present, it is evident that soluble Prussian blue contains the ferrocyanide complex.

When a solution containing potassium ferricyanide and ferric chloride is acted on by free hydroxylamine, soluble Prussian blue alone is formed; from this it follows that soluble Turnbull's blue is identical with soluble Prussian blue; in other words, Turnbull's blue is not a ferrous ferricyanide. Ferrous cyanide is not obtained by adding ammonia to a solution containing ferrous chloride and prussic acid; the precipitates thus obtained on oxidation are converted into complex substances in which the atomic ratio of iron to carbon is

1 : 3, and not 1 : 2 as it would be were the original precipitate ferrous cyanide.

The *compound* $Fe_2C_6N_6NH_4,1\frac{1}{2}H_2O$ is obtained by oxidising the precipitate formed by the interaction of ferrous chloride (1 mol.), hydrocyanic acid (6 mols.), and ammonia (4 mols.), and similarly the *compound* $Fe_2C_6N_6H,2H_2O$ when the proportions, ferrous chloride (1 mol.), prussic acid (6 mols.), and ammonia (2 mols.) are used. These compounds are blue powders, decomposed by 4% ammonia in four minutes at 15°, insoluble in water, soluble, however, in a saturated aqueous solution of oxalic acid. Similar compounds were obtained by using hydroxylamine instead of ammonia.

When the *compound*, $Fe_2C_6N_6H_2$, obtained by boiling an aqueous solution of hydroferrocyanic acid with exclusion of air, is oxidised, a blue *compound*, $Fe_2C_6N_6H,H_2O$, insoluble in water, oxalic acid, and ammonium oxalate solutions, is formed. Although similar to Williamson's violet, it differs from it in that it is decomposed by ammonia. Attempts to prepare a Williamson's violet containing sodium were unsuccessful. The compound, $Fe_2C_6N_6K_2$, obtained as a residue in the preparation of hydrocyanic acid, is also formed by heating a solution of potassium ferrocyanide with excess of oxalic acid.

All soluble blue iron-cyanogen compounds of the general formula FeC_6N_6FeMe,xH_2O are reduced by ammonium oxalate in direct sunlight to a yellowish-white substance which is converted by hydrogen peroxide into Monthier's blue (Berzelius, *Jahresb.*, **27**, 173). The latter compound, $Fe_2C_6N_6NH_4,H_2O$, is, however, best prepared by oxidising with hydrogen peroxide the green precipitate obtained by acting on a solution containing potassium ferrocyanide, ammonium chloride, and ammonia with fine iron wire; it dissolves in water and oxalic acid, forming blue solutions, not, however, in ammonium tartrate solution; it is precipitated from its aqueous solution by ammonium oxalate, and is decomposed by 4% ammonia in five to seven minutes. It is therefore very similar to the blue iron-cyanogen compound obtained from an acidified solution containing potassium ferrocyanide (1 mol.) and a ferrous salt (1 mol.) (compare Abstr., 1905, i, 756). A compound of the same formula, $Fe_2C_6N_6NH_4,H_2O$, is obtained by oxidising in a neutral solution the compound formed by the reduction of Prussian blue with hydrogen sulphide. Robiquet [Dammer, *Handbuch III.* (1893), 364] considered the substance obtained by reducing Prussian blue with hydrogen sulphide to be ferrous cyanide, but this cannot be correct, since by oxidation in neutral solution only an oxycyanide and not the above compound, $Fe_2C_6N_6NH_4,H_2O$, should be obtained.
W. H. G.

Conditions of Stability of the Carbylamines. H. GUILLEMARD (*Compt. rend.*, 1907, **144**, 141—143. Compare this vol., ii, 141).—When a mixture of excess of ethylcarbylamine with a small quantity of ethyl iodide is kept at the ordinary temperature for a prolonged period, a brown, crystalline additive compound, 2EtNC,3EtI, may be isolated by distillation in a vacuum. It is very soluble in water and organic solvents, and is easily decomposed by heat, by acids, and by alkalis; with the latter the products include diethylamine and alkali oxalate. If the action takes place at a high temperature, a tarry product, apparently either a mixture of the above compound and a polymeride of the carbylamine or a compound of this polymeride with ethyl iodide, is obtained.

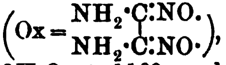
The carbylamines are instantly destroyed by normal alkyl sulphates and by those sulphovinates which are not strictly neutral. They combine with metallic cyanides, giving compounds the stability of which varies with the cyanide employed, but all are dissociated by heat. The silver compound, AgNC,CNEt, which can be considered as the ethyl ester of hydroargentocyanic acid, dissociates into silver cyanide and ethyl carbylamine below 140°. Above 140° a mixture of nitrile and carbylamine is formed, the proportion of nitrile increasing with rise of temperature.

The silver compound, when heated to 160° in a sealed tube for four hours, is completely converted into silver cyanide and the nitrile.

When the carbylamines are heated in sealed tubes, the molecular weight rises gradually at temperatures from 100° to 160° and falls between 160° and 240°, whilst the quantity of nitrile formed increases regularly from 140° to 240°, at which temperature the conversion into nitrile is complete. Hence it follows that, on heating, the carbylamine polymerises first, and the product dissociates into carbylamine and nitrile, the proportion of the latter increasing as the temperature is raised, because the reaction is not reversible. A small quantity of the polymeride was isolated as a very explosive, oily substance, which from a cryoscopic determination appears to be termolecular.

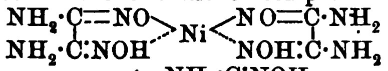
The conclusion is drawn that in their preparation the carbylamines may combine with the alkylating agent, and under the action of heat may give rise to nitriles after polymerisation or combination with the cyanide. E. H.

Complex Compounds of Oxalenediamino-oxime. LEO TSCHUGAEFF and JAC. SURENJANZ (*Ber.*, 1907, **40**, 181—185. Compare Abstr., 1905, i, 743; 1906, i, 814).—Oxalenediamino-oxime, which resembles on the one hand the ethylenediamines in having two amino-groups in the $\alpha\beta$-position to each other, and, on the other hand, the α-dioximes in having two oxime groups in the same relative positions, has, as was to be expected, a strong tendency to the formation of two series of complex metallic compounds. In the present paper the nickel compounds are described.

The action of slightly more than 2 mols. of oxalenediamino-oxime on nickel acetate (1 mol.) in aqueous solution, or on other nickel salts in presence of ammonia, pyridine, or ammonium acetate, leads to the formation of the *compound*, $Ni(OxH)_2,2H_2O$  $\left(Ox = \begin{matrix} NH_2\cdot C{:}NO\cdot \\ | \\ NH_2\cdot C{:}NO\cdot \end{matrix}\right)$, which crystallises in orange-red needles, loses $2H_2O$ at 110°, and decomposes with explosive violence at about 270°. It dissolves in dilute mineral acids or acetic acid, forming a blue solution, is decomposed by an excess of mineral acid, gives a brownish-red coloration with concentrated aqueous alkalis, yields nickel sulphide when treated with hydrogen or ammonium sulphide, and on solution in aqueous potassium cyanide forms oxalenediamino-oxime and potassium nickel cyanide.

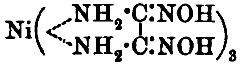
In concentrated solution and in presence of acetic acid, 1 mol. of nickel chloride reacts with 3—4 mols. of oxalenediamino-oxime, forming the *chloride*, $Ni(OxH_2)_3Cl_2$, which crystallises in bluish-violet needles, decomposes suddenly at 230°, and is moderately stable in acid solutions; towards ammonium sulphide, excess of mineral acid, or potassium cyanide solution it behaves in the same manner as the orange-red compound into which it is converted by the action of water. Both chlorine atoms are ionised, being removed as silver chloride on addition of silver nitrate. The nitrate, $Ni(OxH_2)_3(NO_3)_2$, forms bluish-violet prisms, behaves towards reagents in the same manner as the chloride, and yields the whole of its nitric acid as nitron nitrate on addition of nitron acetate solution (Busch, Abstr., 1900, ii, 282).

The structures of the two nickel compounds are discussed, and concluded to be



$$\begin{matrix} NH_2\cdot C{=}NO \\ | \\ NH_2\cdot C{:}NOH \end{matrix} \!> Ni < \begin{matrix} NO{=}C\cdot NH_2 \\ | \\ NOH{:}C\cdot NH_2 \end{matrix}$$

and



$$Ni\left(< \begin{matrix} NH_2\cdot C{:}NOH \\ | \\ NH_2\cdot C{:}NOH \end{matrix}\right)_3$$

respectively. G. Y.

Study of a Case of Isomerism among the Oxonium Compounds of Grignard and Baeyer. WLADIMIR TSCHELINZEFF (*Compt. rend.*, 1907, 144, 88—90).

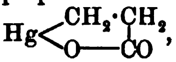
—If the oxonium derivatives obtained by the condensation of organomagnesium compounds with ethers possess the structure suggested by Baeyer (Abstr., 1902, i, 355), isomerides of the types $OR_2X\cdot MgR'$ and $ORR'X\cdot MgR$ should be possible, and the author has prepared a series of compounds in which $R = C_2H_5$ and $R' = C_3H_7$, C_4H_9, C_5H_{11}, or C_6H_5 by adding one equivalent of the ether to the organomagnesium compound in benzene solution, and has measured the heat developed when the compounds are decomposed by water. Ethylmagnesiumethylpropyloxonium iodide, $OEtPrI\cdot MgEt$, obtained from ethyl propyl ether and magnesium ethyl iodide, has a heat of decomposition 62·3 cal., and the isomeride propylmagnesiumdiethyloxonium iodide, $OEt_2I\cdot MgPr$, has 62·5 cal.; similarly, ethylmagnesiumethyl*iso*butyloxonium iodide, $C_4H_9\cdot OEtI\cdot MgEt$, has 58·7 cal., and *iso*butylmagnesiumdiethyloxonium iodide has 60·2 cal.; ethylmagnesiumethyl*iso*amyloxonium iodide, $C_5H_{11}\cdot OEtI\cdot MgEt$, yields ethane when decomposed by water with a heat development of 62·9 cal., whilst the decomposition of *iso*amylmagnesiumdiethyloxonium iodide, $OEt_2I\cdot Mg\cdot C_5H_{11}$, is not accompanied by any evolution of gas, and the heat equivalent is 60·5 cal.; ethylmagnesiumphenylethyloxonium iodide, $OEtPhI\cdot MgEt$, is decomposed by water with evolution of ethane and a heat equivalent of 62·1 cal., and phenylmagnesiumdiethyloxonium iodide, $OEt_2I\cdot MgPh$, yields benzene on decomposition with water and a heat equivalent of 59·2 cal.

No conclusions as to the possible isomerism among the oxonium derivatives can be drawn from the results of the thermochemical investigation given above, as the thermal values are practically identical, but the nature of the products of decomposition show that the compounds do show isomerism of the type suggested by Baeyer.

M. A. W.

β-Mercuridipropionic Acid. Emil Fischer (*Ber.*, 1907, 40, 386—389. Compare Pesci, Abstr., 1901, i, 624).—This work was undertaken to fill a gap in the organo-mercuric derivatives amongst which previously no compounds of the fatty acids have been described.

Ethyl β-mercuridipropionate, $Hg(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, prepared by shaking ethyl β-iodopropionate with sodium amalgam in cooled ethereal solution, is obtained on evaporation of the ethereal solution in a vacuum as a yellow oil having an unpleasant odour. The *acid*, $Hg(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$, formed by shaking the ester with *N*-sodium hydroxide, crystallises from water in slender, colourless, odourless prisms, m. p. 148·5—149·5° (corr.), can be titrated with sodium hydroxide in presence of phenolphthalein, is readily decomposed by halogens or strong acids, and yields with iodine mercuric iodide, with a limited amount of boiling hydrobromic acid, a crystalline *substance* which may be *bromomercuripropionic acid*, or with an excess of hydrobromic acid mercuric bromide; when warmed gently with iodine in aqueous potassium iodide solution, mercuridipropionic acid yields a dark crystalline *periodide*. The *copper*, *lead*, and *silver* salts are described.

β-Mercuridipropionic acid is decomposed by water at 100° yielding propionic acid and the *anhydride* of β-hydroxymercuripropionic acid,  $Hg\Big<\begin{matrix}CH_2{\cdot}CH_2\\ O\text{—}CO\end{matrix}$, which separates in colourless crystals, becomes grey at about 190°, gradually decomposes at higher temperatures, and is soluble in dilute alkalis or warm dilute acids.

G. Y.

The Benzene Nucleus, its Reactivity, and the Valency Strength of its Substituting Groups and of Carbon. Julius Obermiller (*J. pr. Chem.*, 1907, [ii], 75, 1—61. Compare Flürscheim, Abstr., 1905, i, 614).—The argument of this theoretical paper is based on the following conceptions of valency.

(1) The valencies of an atom are the directions in which the force constituting the total affinity of the atom acts. The valencies act in straight lines but may be diverted to a certain extent. The valency of an atom is the number of directions in which the affinity acts and the number of valencies of other elements which must be neutralised in the formation of a chemical compound.

(2) The total affinity of the atom varies for different elements and is not proportional to the valency, that is, the average affinities of the valencies of the atom are different for different elements.

(3) It is not necessary in a chemical compound that the total affinity of an atom should be completely neutralised; any excess of affinity expresses itself in the so-called secondary valencies, partial valencies, indirect linkings, &c.

(4) The valencies of a multivalent atom may vary in strength, the distribution of the total affinity of the atom depending chiefly on the strength of the valencies neutralised.

(5) The mutual attraction of chemical affinities is to be considered as a special case of mass attraction, $m.m'/r^2$. The force forming the linking is the product of the two valencies which are mutually neutralised and which are not necessarily of the same strength.

(6) The affinity necessary for the formation of a given linking is constant within certain limits, outside of which unstable compounds are formed or combination does not take place; this necessary affinity varies for different combinations of atoms and depends on the manner in which the remaining valencies of the atoms concerned are occupied. It follows that in a combination of two atoms the affinity of the one atom must be the greater the less that of the second valency forming the linking. In the combination *AB*, the affinity required of *B* in consequence of that of *A* to make the combination, is termed the "valency need-*B*" of the atom *A*, and the possibility of measuring it is discussed.

It is suggested that the "valency need-*C*" of the carbon atom is greater than the affinity of the average carbon valency, when it follows that in the centric formula for benzene, which agrees best with the above conceptions of valency, with the direct formation of substitution compounds, and the nature of partially reduced benzene derivatives, more than half of the total affinity of the six carbon atoms is required for the formation of the ring, and after expenditure of sufficient affinity for the union with the six hydrogen atoms there remains for the centric valencies less affinity than is necessary for the formation of true C–C linkings; the centric valencies are considered to be of the nature of *pseudo-para*-linkings. If now one of the hydrogen atoms is substituted by a group requiring a greater carbon affinity for combination, the remaining three valencies, forming the two *ortho-* and the one *para*-linkings, of the carbon atom to which the new group is attached, must be weakened with the effect of rendering the two *o-* and the *p*-hydrogen atoms less firmly attached to the nucleus and therefore more reactive. It is for this reason that the introduction of a second substituting group tends to take place in the *o-* and *p*-positions. *Meta*-substitution is considered to be a consequence of steric hindrance. The stability of a benzene derivative must diminish with increasing "valency need" of the substituting group, hence the great stability of benzene is in agreement with the order of "valency need-*C*" represented by the series given below.

These considerations are shown to apply also to the orientation of substitution in pyridine, naphthalene, and anthracene, and to the mutual influence on each other of two or more substituting groups as modified by their relative positions in the benzene nucleus.

If the orientation of a group is influenced in two directions by two substituting groups already present in the benzene nucleus, the influence of the stronger of these will predominate to the greater extent the more the two groups differ in "valency need-*C*" and the more easily the introduction of the third group takes place. That the stronger substitution group is that with the greater "valency need" follows from the above exposition of the affinity equilibrium of the benzene nucleus and its disturbance by substitution. From consideration of a number of cases of substitution it is shown that the "valency need-*C*" diminishes from N‴ to H in the series: N‴, C^{IV}, NO_2, SO_3H, OH, NH_2, Cl(Br), CH_3, H.

The "valency need-*C*" of carbon being greater than the average affinity of a carbon valency, the stability of methane and its homologues results from the small "valency need-*C*" of hydrogen, on the other hand, for the same reason, whilst in tetranitromethane sufficient carbon affinity is at the disposal of each nitro-group, hexanitroethane must be unstable if capable of existence (compare Hantzsch, Abstr., 1906, i, 617). The properties of acetylene and of the cyanogen group, the existence of both tetraphenylmethane and triphenylmethyl, and the instability of two hydroxyls when attached to the same carbon atom are discussed from the author's point of view.

G. Y.

[Oxidation of Aromatic Hydrocarbons and their Derivatives with Manganese Disulphate.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 175295).—Manganese disulphate, $Mn(SO_4)_2$, in acid solution has the property of oxidising the methyl group of toluene and its homologues and derivatives in such a way that aldehydes and, finally, carboxy-acids are obtained. The manganous sulphate resulting from the oxidation can be readily reconverted into the disulphate by electrolytic oxidation. Toluene when oxidised at 40—50° furnishes an almost quantitative yield of benzaldehyde, and when the oxidation is effected at a higher temperature with a further quantity of manganese disulphate, benzoic acid is obtained finally. Benzyl alcohol and chloride may also be oxidised in this manner to yield benzaldehyde and even benzoic acid. G. T. M.

Oxidation of Substituted Aromatic Hydrocarbons. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 174238).—*o*-Chlorotoluene is readily oxidised to *o*-chlorobenzaldehyde when suspended in 60—65% sulphuric acid at 50° and treated gradually with cerium dioxide, the temperature being slowly raised to 90°. The product now contains a white, pasty mass of cerous sulphate, mixed with *o*-chlorobenzaldehyde and a small quantity of *o*-chlorobenzoic acid, the yield of aldehyde being 66%.

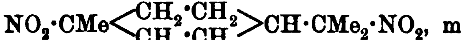
The *o*- and *p*-nitrotoluenes are similarly oxidised at 80—85°, but in this case more of the corresponding nitrobenzoic acids are produced.

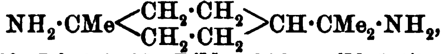
The anthracenesulphonic acids are readily oxidised in this way to anthraquinonesulphonic acids even at the ordinary temperature.

G. T. M.

The Two Modifications of *o*-Nitrotoluene. EMIL KNOEVENAGEL (*Ber.*, 1907, 40, 508—517. Compare Abstr., 1903, i, 785).—The existence of *o*-nitrotoluene in two forms (compare Ostromisslensky, this vol., i, 120) had been discovered by Schmidt and Berndt in 1903 in the Griesheim-Elektron works. The author also showed in 1904 that the α-form (m. p. $-9{\cdot}4°$) is transformed exothermally at low temperatures into the β-form (m. p. $-3{\cdot}6°$). The two modifications exhibit differences in the liquid as well as in the solid state, and are therefore regarded as chemical isomerides and as instances of motoisomerism.

The author proceeds to develop his theory of motoisomerism. The fact that the viscosity of freshly distilled nitrobenzene differs from that of nitrobenzene, determined five hours after distillation, is attributed by the author to motoisomerism. C. S.

Nitro-derivatives in the Menthane Series. III. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, i, 449—453. Compare Abstr., 1904, i, 513).—Menthane was heated with nitric acid, D 1·1 at 115—120°, in a sealed tube. Three crystalline dinitro-compounds were obtained, melting respectively at 98—100°, 92—95°, and 75—85°. The first fraction yielded *dinitromenthane*, $C_{10}H_{18}(NO_2)_2$, probably  $NO_2\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot NO_2$, m. p. 107·5—108·5°. It is readily soluble in benzene, sparingly so in ether, and does not distil but commences to decompose at 210°. Zinc dust and acetic acid reduce it to the corresponding *diamine*, probably

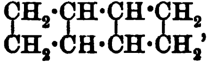


$$NH_2\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2\cdot NH_2,$$

b. p. 231—233°, D_0^0 0·9263, $D_0^{17\cdot5}$ 0·9108, $n_D^{17\cdot5}$ 1·47955, a colourless liquid which does not solidify at −8°. The *hydrochloride* and *sulphate* are described. The *dibenzoyl* derivative, $C_{10}H_{18}(NHBz)_2$, m. p. 232·5—233·5°, crystallises from alcohol in small needles. Z. K.

[Nitration of 3 : 4-Dichlorobenzenesulphonic Acid.] AKTIENGESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 175022. Compare Abstr., 1904, i, 1065).—The nitration product of 3 : 4-dichlorobenzenesulphonic acid in concentrated sulphuric acid is poured on to ice and the nitro-sulphonic acids salted out in the form of their sodium salts. The mixed salts, when redissolved in water and allowed to crystallise, yield a crop of the less soluble sodium 4 : 5-dichloro-2-nitrobenzenesulphonate, whilst an isomeric salt of the nitro-sulphonic acid, containing the nitro-group either in position 3 or 6, remains in the mother liquors. The calcium, barium, and zinc salts of the latter acid are generally more soluble than those of 4 : 5-dichloro-2-nitrobenzenesulphonic acid. On reducing the mixture of these two nitro-acids with iron and dilute acetic acid, the corresponding amino-sulphonic acids are obtained. 4 : 5-Dichloroaniline-*o*-sulphonic acid is by far the less soluble and is precipitated from an acidified solution of its sodium salt. The isomeric acid remains in the mother liquors and is obtained on concentration. When successively diazotised and treated with alkali, one of the chlorine atoms of this more soluble acid is replaced by hydroxyl, showing that the amino-group was originally in the ortho-position to one of the chlorine atoms. It is on account of this reaction that the nitro-group is assumed to enter position 3 or 6. G. T. M.

Unsaturated Acids of the Sorbic Series and their Conversion into Cyclic Hydrocarbons. III. OSCAR DÖBNER (*Ber.*, 1907, **40**, 146—147).—The hydrocarbon, C_8H_{12}, previously termed *cyclo*octadiene (Abstr., 1902, i, 598) is not identical with Willstätter and Veraguth's *cyclo*-octadiene (Abstr., 1905, i, 515). As the latter possesses the properties of an unsaturated compound it is probable that the hydrocarbon obtained from β-vinylacrylic acid has the constitution



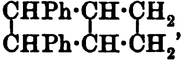
$$\begin{array}{c} CH_2\cdot CH\cdot CH\cdot CH_2 \\ |\qquad\;|\qquad|\qquad| \\ CH_2\cdot CH\cdot CH\cdot CH_2 \end{array},$$

and is termed tricyclo*octane*.

J. J. S.

Unsaturated Acids of the Sorbic Series and their Conversion into Cyclic Hydrocarbons. IV. Oscar Döbner and G. Schmidt (*Ber.*, 1907, **40**, 148—152. Compare Abstr., 1902, i, 598; 1904, i, 149, and preceding abstract).—When the yellow modification of cinnamylidenemalonic acid is heated with anhydrous barium hydroxide, it yields phenyl*cyclo*butene, m. p. 25°, b. p. 118—122°/12 mm., together with a considerable amount of diphenyl*tricyclo*-octane, b. p. 204—206°/10 mm., and a small amount of a hydrocarbon, $C_{30}H_{30}$. The last is a viscous liquid and is not attacked by bromine or permanganate.

The colourless cinnamylidenemalonic acid, m. p. 178° (Liebermann, Abstr., 1895, i, 470), when treated in the same manner yields considerable amounts of diphenyl*tricyclo*octane and small amounts of the hydrocarbon, $C_{30}H_{30}$, together with *diphenyl*dicyclo*hexane*,



$$\begin{array}{c} CHPh\cdot CH\cdot CH_2 \\ |\qquad\quad|\qquad| \\ CHPh\cdot CH\cdot CH_2 \end{array},$$

m. p. 56°, b. p. 212—215°/12 mm., and an unsaturated hydrocarbon, α-phenyl-$\Delta^{\alpha\gamma}$-butadiene, $CHPh{:}CH\cdot CH{:}CH_2$, b. p. 93—95°/12 mm., the tetrabromide of which melts at 150° (Klages, Abstr., 1902, i, 669; Riiber, 1903, i, 471).

J. J. S.

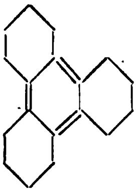
Synthesis of Aldehydes and Ketones from *as*-Disubstituted Ethylene Glycols and their Ethers. A Correction. Richard Stoermer (*Ber.*, 1907, **40**, 488—489).—It was stated (Abstr., 1906, i, 581) by the author that when phenoxyditolylethylene was heated with alcoholic potassium hydroxide at 240°, di-*p*-tolylethylene was formed together with the corresponding ethoxy-compound. Di-*p*-tolylethylene was described as an oil, b. p. 186°/20 mm. This oil is, however, a mixture of ditolylethylene and ditolylmethane.

Di-*p*-tolylethylene had previously been described correctly by Bistrzycki and Reintke as a solid, m. p. 61°.

A. McK.

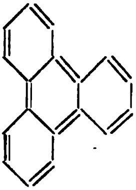
Pentaphenylethane and Hexaphenylethane. Alexei E. Tschitschibabin (*Ber.*, 1907, **40**, 367—369. Compare Abstr., 1905, i, 125; Flürscheim, *ibid.*, 614; Hantzsch, Abstr., 1906, i, 617).—Gomberg and Cone's pentaphenylethane (Abstr., 1906, i, 821), m. p. 178—179° (decomp.), determined in an atmosphere of carbon dioxide, which behaves at the ordinary temperature as a saturated hydrocarbon, when heated alone or in nitrobenzene solution, decomposes into tetraphenylethane and triphenylmethyl, and absorbs oxygen. When heated with hydrogen chloride in benzene solution at 150° with exclusion of air, it yields tetraphenylethane, triphenylmethane, and triphenylmethyl chloride. The decomposition in question must result from a weakening of the linking between the diphenylmethyl and the triphenylmethyl groups of the pentaphenylethane; this behaviour resembles closely that of triphenylmethyl which consequently is considered to be hexaphenylethane. Schmidlin's supposed stable hexaphenylethane (this vol., i, 26) was probably impure tetraphenylethane. The experimental results described are opposed to Vorländer's view that two hexaphenylethanes, a stable and a labile form, are capable of existence. G. Y.

Condensation of *cyclo*Hexanone. Carl Mannich (*Ber.*, 1907, 40, 153—158).—*cyclo*Hexanone yields condensation products in much the same manner as aliphatic ketones (compare Wallach, Abstr., 1896, i, 572; 1897, i, 425). A condensation, similar to the formation of mesitylene from acetone, occurs when *cyclo*hexanone is boiled for some ten to twelve hours with its own weight of concentrated sulphuric acid and 2·5 times its weight of methyl alcohol. The product, *dodecahydrotriphenylene*, the yield of which is some 6%, crystallises from benzene in large, compact prisms, m. p. 232—233°. It may be sublimed in an atmosphere of carbon dioxide or hydrogen. When heated with fuming nitric acid at 180° it yields mellitic acid.



Other products formed during the condensation are a ketone, $C_{12}H_{18}O$, probably identical with that obtained by Wallach (*loc. cit.*), and yielding a *semicarbazone*, m. p. 175—177°, and a *ketone*, $C_{18}H_{26}O$, b. p. 214—217°/15 mm. The latter condenses with guanidine, and the condensation product yields a *picrate*, $C_{25}H_{33}O_7N_7$, m. p. 203° (decomp.). J. J. S.

Triphenylene. Carl Mannich (*Ber.*, 1907, 40, 159—165).—*Triphenylene* is formed when dodecahydrotriphenylene (preceding abstract) is distilled with zinc dust in an atmosphere of hydrogen. It may be isolated in the form of its *picrate*. The hydrocarbon crystallises from benzene or alcohol in colourless needles, m. p. 198—198·5°. A better yield is obtained when the dodecahydro-compound is passed over a layer of copper in an atmosphere of carbon dioxide at 450—500°. When completely oxidised, it yields mellitic acid. With chromic acid, it is oxidised to a mixture of quinones, and with fuming nitric acid yields a *trinitro*-derivative, $C_{18}H_9(NO_2)_3$, which crystallises from nitrobenzene in pale yellow, slender needles, and darkens at 335° without melting. The hydrocarbon is identical with the triphenylene obtained in minute quantities by Schmidt and Schultz (Abstr., 1881, 435). J. J. S.



Use of Acetic Anhydride in Nitrating. Kennedy J. P. Orton (*Ber.*, 1907, 40, 370—376. Compare Trans., 1902, 81, 806; Witt and Utermann, this vol., i, 27).—Nitric acid for use in nitrating in acetic anhydride is freed from nitrous acid by treatment with a limited quantity of carbamide nitrate.

Nitroamines are obtained in a 90% yield, together with nitro-compounds and diazo-salts, from anilines having one or both *o*-hydrogen atoms present if the amine dissolved in glacial acetic acid is run into a mixture of acetic anhydride and nitric and glacial acetic acids cooled in ice-water. The presence of nitrous acid is necessary to the nitration of dialkylanilines, intermediate nitroso-derivatives probably being formed.

Nitrotoluene has been prepared in a quantitative yield by nitration of toluene in presence of acetic anhydride; results are quoted showing that the function of the acetic anhydride is to combine with the water present in the nitric acid and formed during the reaction. Under the same conditions benzoic acid yields *m*-nitrobenzoic acid. G. Y.

Electrochemical Reduction of *o*-Nitroacetanilide. KURT BRAND and EDWARD STOHR (*Ber.*, 1907, **40**, 364. Compare this vol., i, 100).—References are given to two other *o*-nitrosoanilines which had been overlooked by the authors. W. R.

Phenylbiurets and the Biuret Reaction. HUGO SCHIFF (*Annalen*, 1907, **352**, 73—87. Compare Abstr., 1902, i, 429).—By acting on phenylbiuret with aniline, Weith (Abstr., 1878, 141) obtained a compound which he describes as diphenylbiuret; it is shown that this compound is really *s*-diphenylcarbamide. When heated in sealed tubes with carbonyl chloride dissolved in toluene, the latter substance is converted into *s*-diphenylbiuret. Pickard and Carter (Trans., 1901, **79**, 841; 1902, **81**, 1563), by acting on acetylphenylhydroxyloxamide with dilute ammonia, obtained a compound which they thought to be phenylbiuret; this substance is really *as*-phenylbiuret; it crystallises in silvery scales, m. p. 167°, and does not give the biuret reaction; at the same time the following by-products are formed: monophenylcarbamide, oxanilide, *s*-diphenylbiuret, and ammonium oxanilate. When *s*-diphenylcarbamide is heated with carbamide, cyanuric acid is formed together with only small quantities of biuret and monophenylcarbamide; that only small quantities of the last are obtained is probably due to the fact that when heated this compound is partially converted into carbamide and *s*-diphenylcarbamide. The author's original supposition (compare Abstr., 1897, i, 144) that asymmetrically substituted biurets, even when only one of the amido-hydrogen atoms is substituted, do not give the biuret reaction, although true in most cases, has not been found to hold good in all cases. After mentioning the cases in which his proposition fails, the author concludes by putting forward the suggestion that only those reactions which are obtained with amino-amides or diamides derived from the parent substances, biuret, oxamide, and malonamide, with copper or nickel salts, should be known as biuret reactions.

W. H. G.

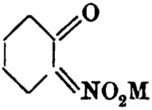
Action of Phosphorus Pentabromide on Phenol Ethers. LOUIS HENRY (*Ber.*, 1907, **40**, 243—244).—A claim for priority (compare *Ber.*, 1869, **2**, 710; Autenrieth and Mühlinghaus, this vol., i, 31). C. S.

Isomerism of the Salts of Nitrophenols and the Existence of Metaquinonoid Compounds. ARTHUR HANTZSCH (*Ber.*, 1907, **40**, 330—351. Compare Abstr., 1906, i, 352, 353).—Two series of coloured alkali salts of nitrophenols have been prepared, one yellow, the other red; the red salts are usually unstable and could not be obtained pure. Colourless 2 : 4 : 6-tribromo-3 : 5-dinitrophenol, however, gives a yellow and a red potassium salt of the same composition and of the same molecular weight and electrical conductivity. Although many of these salts crystallise with water or alcohol, their colour is not dependent on the water or alcohol of crystallisation as this may be removed from the red or yellow potassium salts of tribromonitrophenol without any alteration in colour. The fact that the red ammonium salt of *o*-nitrophenol when dehydrated is yellow and the orange-yellow potassium salt, red, whereas, precisely the reverse is the case with the corresponding salts of 2 : 6-dinitro-*p*-cresol, shows that these are the stable salts under these conditions and that isodynamic change has occurred during the dehydration. The author concludes that the two series of differently coloured salts obtained from colourless nitrophenols have different constitutions and that their colour is independent of the alkali metal present as all the yellow and all the red salts are almost of the same colour intensity.

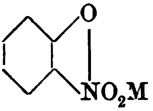
The yellow and red salts are morphologically different (compare Rabe, Abstr., 1901, i, 697), and generally either the red or the yellow salt is alone formed, but with *m*-nitrophenols, orange salts are obtained which are of the nature of solid solutions of the red and yellow varieties.

The nitro-group not conferring colour on a compound, it follows that the real nitrophenols should be colourless, and their salts must possess the constitution represented by either of the two formulæ:

(I)

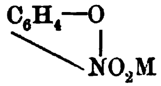


(II)



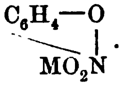
As an analogous series of coloured salts of dinitroparaffins has been prepared, the change in colour from red to yellow and conversely cannot be due to changes in the nature of the benzene ring. Again, the isomerism existing amongst these salts is not due to one salt being represented in constitution by the first, and the other by the second formula, otherwise benzene derivatives free from nitrogen should give also yellow and red salts. This is not the case (compare Abstr., 1906, i, 856) and these salts are concluded to be structurally identical; they are therefore stereoisomeric and are represented by *syn*- and *anti*-configurations. By analogy with the red and yellow salts of benzene diazosulphonates, the red salt is given the *syn*-formula (I), the yellow the *anti*-formula (II), thus:

(I)



$$\begin{array}{l} C_6H_4—O \\ \diagdown \quad\quad | \\ \quad\quad NO_2M \end{array}$$

(II)

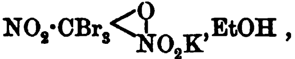


$$\begin{array}{l} C_6H_4—O \\ \quad \diagdown \; | \\ MO_2N \end{array}$$

The determination of the actual configuration is not yet possible.

The existence of two classes of coloured *m*-nitrophenol salts is held to be a proof of their metaquinonoid character, although metaquinones are possibly not capable of existence.

[With N. ROSANOFF.]—The m. p. of 2 : 4 : 6-tribromo-3 : 5-dinitrophenol is 188°, not 194° (compare Jackson and Warren, Abstr., 1894, i, 176), and its *acetyl* derivative forms colourless needles, m. p. 164°. The separation of the orange mixed *potassium* salt,



$$NO_2\cdot CBr_3<\begin{matrix}O\\ NO_2K\end{matrix},EtOH\,,$$

into the *lemon-yellow* and *red isomerides* must be carried out in absolutely dry solvents. By addition of dry ether and benzene to an alcoholic solution and spontaneous evaporation in a vacuum over sulphuric acid, the yellow salt crystallises out first. From the mother liquor the mixed salt is next precipitated, and, finally, the vermilion-red salt is obtained. After recrystallising the salts two or three times, a yield of 2% of the yellow salt and 4—5% of the red is obtained. The two salts are microcrystalline and their solutions are yellow and dark orange respectively; the solutions gradually change in colour, due to isodynamic change. When in *N*/10 solution the yellow solution freshly prepared absorbs light up to a wave length of 508, the dark orange to 523, whereas the orange mixed salt gives absorption up to 521. By following the change in the spectroscope, the yellow solution had changed its absorption from 508 to 519 in ten hours, and in 2·5 months the less unstable red solution from 528 to 523. There is therefore in the equilibrated orange mixture roughly 66% of the red salt. These salts are also labile in the solid state.

The *cæsium* salts are the only alkali salts in addition to the potassium capable of separate existence and can be separated into a yellow and red variety from the orange mixture. The red salt is much less stable than the corresponding potassium salt.

The *sodium* salt, prepared either at the ordinary temperature or at − 75°, is yellow and gives a yellow aqueous solution, the *lithium* and unstable *ammonium* salts are also yellow. The following metals give mixed salts: *rubidium*, *barium*, *calcium*, *thallium*, as also the *pyridine* salt. These salts in solution do not show isodynamic change.

The *potassium* salt is the only salt of 3 : 5-dinitrophenol to give an indication of two forms, as it alters its colour on heating to 100°; the mixed orange salt could not be separated. The *rubidium* salt is orange; the *barium*, light orange; the *sodium*, *lithium*, *ammonium*, and *silver* salts are pure yellow.

[With E. BORCHERS.]—The *potassium* and *sodium* salts of *m*-nitrophenol are yellow at low temperatures, but change in solution at 0° into the red salt. These salts could not be isolated. An ethereal or benzene solution of 1 mol. of *m*-nitrophenol and 1 mol. of ammonia is practically colourless, but excess of ammonia precipitates the orange-coloured *ammonium* salt.

The *potassium* and *sodium* salts of *o*-nitrophenol when prepared at low temperatures are lemon-yellow, but these salts are very unstable, giving immediately the scarlet salts at − 75° with excess of ethoxide. The yellow *ammonium* salt is only stable at low temperatures; at the ordinary temperature it is orange, and scarlet plates have been obtained from solid *o*-nitrophenol (compare Merz and Ris, *Ber.*, 1886, **19**, 1752).

On the other hand, the salts of *p*-nitrophenol behave differently from those of *o*-nitrophenol. The red salts are the exception; at low temperatures, yellowish-white salts are obtained.

The ethyl ester of 2 : 6-dinitro-*p*-cresol is colourless. The potassium and sodium salts of this cresol are orange-yellow and orange when anhydrous; when hydrated they are red. The ammonium salt is red when anhydrous and orange-yellow when hydrated; the *cæsium*, *barium*, and *calcium* salts are anhydrous and orange-yellow, the *silver* salt is red (compare Städel, Abstr., 1883, 662).

Pentamethylenediamine picrate when first prepared is red, but in a desiccator it becomes yellow. At - 80° ammonium picrate is red, at the ordinary temperature yellow. When prepared in benzene or ether solution, the potassium salts are vermilion-red, the potassium salt becoming yellow. The sodium salt is more stable, but by washing with alcohol below 0° it also becomes yellow. W. R.

Acyl Derivatives of *o*- and *p*-Aminophenol. J. BISHOP TINGLE and L. F. WILLIAMS (*Amer. Chem. J.*, 1907, **37**, 51—71).—*o*-Benzoylaminophenyl benzoate, m. p. 180°, prepared by the action of benzoyl chloride on *o*-acetylaminophenol, crystallises in white, slender needles. The following compounds of *o*-aminophenol are also described. p-*Nitrobenzoyl*-o-*aminophenol*, $NO_2·C_6H_4·CO·NH·C_6H_4·OH$, m. p. 220°, forms small, yellow crystals; its p-*nitrobenzoate*,

$$NO_2·C_6H_4·CO·NH·C_6H_4·O·CO·C_6H_4·NO_2,$$

m. p. 219°, light, feathery crystals. m-*Nitrobenzoyl*-o-*aminophenol*, m. p. 206°, forms small, yellow crystals; the m-*nitrobenzoate*, m. p. 188°, light, flaky plates. *Benzenesulphonyl*-o-*aminophenol*,

$$SO_2Ph·NH·C_6H_4·OH,$$

m. p. 141°, forms small, white needles; its benzenesulphonate,

$$SO_2Ph·NH·C_6H_4·O·SO_2Ph,$$

m. p. 134° (not 81—83°, Georgescu, Abstr., 1900, i, 344), faintly red, columnar crystals.

p-Acetylaminophenol, m. p. 166° (not 179°, Morse, Abstr., 1878, 416), when treated with acetyl chloride, yields the acetate previously obtained by Ladenburg (Abstr., 1877, i, 305) by a less convenient method. *p*-Acetylaminophenol shows a different behaviour with benzoyl chloride from that of the corresponding *o*-derivative, and yields *p*-acetylaminophenyl benzoate, $NHAc·C_6H_4·OBz$, m. p. 166·5°, which forms white, feathery crystals (compare Reverdin, this vol., i, 37). The following compounds of *p*-aminophenol have also been prepared. *p*-Benzoylaminophenol, m. p. 227·5° (not 205—207°, as stated by Smith, Abstr., 1892, i, 490). p-*Nitrobenzoyl*-p-*aminophenol*, $NO_2·C_6H_4·CO·NH·C_6H_4·OH$, m. p. 258°, forms small, lustrous, orange-red, monoclinic crystals; its p-*nitrobenzoate*,

$$NO_2·C_6H_4·CO·NH·C_6H_4·O·CO·C_6H_4·NO_2,$$

m. p. 264°, light yellow, microscopic crystals. m-*Nitrobenzoyl*-p-*aminophenol*, m. p. 215—216°, forms light yellow, slender needles; its m-*nitrobenzoate*, m. p. 264—265°, a light grey powder. By the action of benzenesulphonic chloride on *p*-aminophenol, benzenesulphonyl-*p*-aminophenol is produced, but the di-benzenesulphonyl derivative described by Georgescu (*loc. cit.*) could not be obtained.

Experiments have been made at 0°, at the ordinary temperature, and at 240—250° with the object of obtaining tribenzoyl derivatives of *o*- and *p*-aminophenol, but without success. E. G.

Preparation of Thio-derivatives of Quinol and its Chloro-compounds.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 175070).—*Potassium quinolthiosulphonate* separates as a colourless, crystalline powder on adding aqueous sodium thiosulphate to a warm acetic acid solution of *p*-benzoquinone, and subsequently salting out with potassium chloride. The corresponding *mercaptan*, $SH\cdot C_6H_3(OH)_2$, m. p. 119—120°, is obtained in colourless needles on reducing the preceding compound with zinc dust and an acid. The sodium derivative of the mercaptan, on treatment with iodine, furnishes the *disulphide*, m. p. 185°. The mercaptan and benzoquinone together form the *monosulphide*, m. p. 227—229°. Quinolthiosulphonic acid on oxidation with potassium dichromate yields the corresponding quinonethiosulphonic acid.

Potassium α-quinoldithiosulphonate, obtained from benzoquinone and a larger proportion of sodium thiosulphate, is very soluble in water, but dissolves only sparingly in alcohol. The mercaptan forms colourless leaflets, m. p. 190—192°.

Potassium β-quinolthiosulphonate, isomeric with the preceding salt, was obtained by dissolving benzoquinonethiosulphonic acid in dilute acetic acid at 65—70°, and pouring this solution into aqueous sodium thiosulphate at 10°; on adding potassium chloride the moderately soluble potassium salt separated, and when crystallised from water formed white needles. The mercaptan forms white needles, m. p. 165—166°. These two quinoldithiosulphonic acids when oxidised by acidified dichromate yield the corresponding benzoquinonethio-acids.

Potassium quinoltetrathiosulphonic acid is the ultimate product of the action of excess of thiosulphate on quinol or benzoquinone in the presence of oxidising agents; it forms white, felted needles sparingly soluble in cold and readily so in hot water.

2 : 6-*Dichloroquinol*-3-*thiosulphonic acid*, from dichloroquinol and sodium thiosulphate, forms soluble, yellowish-white needles; the mercaptan has m. p. 171—172°. It is readily oxidised to the corresponding quinone.

Potassium 2 : 6-*dichloroquinoldithiosulphonate* oxidises to a quinone, and yields a mercaptan, m. p. 215°.

Benzoylquinolmercaptan, $C_6H_3(OH)_2\cdot S\cdot CO\cdot C_6H_5$, obtained by mixing benzoquinone and thiobenzoic acid in ethereal solution; m. p. 158—169°; the *tribenzoyl* derivative, $C_6H_3(OBz)\cdot SBz$, m. p. 116—118°.

Quinol xanthate, $C_6H_3(OH)_2\cdot S\cdot CS\cdot OEt$, produced by the interaction of benzoquinone and potassium xanthate, is a green, crystalline powder, m. p. 75—79°.

Thio-derivatives of quinol were also obtained by the interaction of benzoquinone with thiocyanic and trithiocarbonic acids.

G. T. M.

Lupeol. N. H. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 466—470. Compare Likiernik, Abstr., 1891, 551, 1446; Romburgh, Abstr., 1904, i, 905).—Sack's alstol (*Diss.*, *Göttingen*, 1901) is not a pure substance.

The most probable formula for lupeol is $C_{31}H_{50}O$. The benzoate, formed by the action of benzoyl chloride and pyridine on lupeol obtained from djelutung, crystallises in slender, flat needles, m. p. 273—274° (corr.), has $[\alpha]_D +60.75°$ in chloroform solution, and on hydrolysis yields lupeol crystallising in long needles, m. p. 215° (corr.). When treated with bromine in a mixture of glacial acetic acid and carbon disulphide, the benzoate yields two *monobromo*-derivatives, $C_{38}H_{53}O_2Br$, of which the less soluble in acetone separates from ethyl acetate in stout crystals, m. p. 243°, has $[\alpha]_D +44.9°$ in chloroform solution, and on hydrolysis forms benzoic acid and a *bromo-alcohol*. The more readily soluble isomeride crystallises from acetone in leaflets.

The action of bromine on lupeol in carbon disulphide solution leads to the formation of a *monobromo*-derivative, $C_{31}H_{49}OBr$, which crystallises in needles, m. p. 185° (corr.), and has $[\alpha]_D +3.8°$ in chloroform solution.

Lupeol is oxidised by Kiliani's chromic acid mixture (Abstr., 1902, i, 46), yielding *lupeone*, $C_{31}H_{48}O$, which forms rhombo-dipyramidal crystals, m. p. 170° (corr.), has $[\alpha]_D +63.1°$ in chloroform solution, and is reduced to lupeol by sodium and alcohol; hence, if lupeone contains an ethylene linking this cannot be in the $\alpha\beta$-position to the carbonyl group. The *oxime*, $C_{31}H_{49}ON$, crystallises in soft, white needles, m. p. 278.5° (decomp.), and has $[\alpha]_D +29.5°$ in chloroform solution. The action of bromine on lupeone in glacial acetic acid solution leads to the formation of hydrogen bromide and a *dibromo*-derivative, $C_{31}H_{46}OBr_2$, which crystallises in hard needles, m. p. 254° (decomp.), and has $[\alpha]_D +21.4°$ in chloroform solution. The *cyanohydrin*, $C_{32}H_{49}ON$, formed by the action of hydrogen cyanide on lupeone in ethereal solution in presence of a trace of ammonia, crystallises in stout needles, m. p. 194° (decomp.), and when treated with 1 mol. of hydrogen chloride and 1 mol. of ethyl alcohol yields a *product*, m. p. 235°.

Neither lupeol nor its acetate is oxidised by potassium permanganate in boiling acetone solution, whilst the benzoate and lupeone in benzene solution at 40° are not acted on by Kiliani's chromic acid mixture; at higher temperatures lupeone forms acid *products* which cannot be crystallised. When oxidised with potassium permanganate in sulphuric acid solution, lupeol yields a mixture of products from which lupeone alone has been isolated; the action of alkaline permanganate on lupeol leads to complete oxidation.

The *product*, $C_{33}H_{50}O_3$, obtained by oxidation of lupeol acetate with chromic acid in acetic acid solution, does not redden blue litmus, but can be titrated with alcoholic potassium hydroxide in presence of phenolphthalein, and on hydrolysis yields a *product*, $C_{31}H_{50}O_3$, which crystallises in needles, m. p. 263—265°, and behaves towards litmus and phenolphthalein in the same manner as the acetyl derivative. The hydrolysis product forms a *potassium* salt crystallising in needles, and yields a *diacetyl* derivative, $C_{35}H_{54}O_5$, which is formed also directly from the oxidation product.

Lupeol and lupeone both give the reaction for unsaturated compounds with Hübl's iodine reagent. G. Y.

Cholesterol. VIII. Adolf Windaus (*Ber.*, 1907, **40**, 257—261. Compare Abstr., 1906, i, 580).—The oxidation of cholesterol in benzene solution by alkaline potassium permanganate leads to the formation of a crystalline neutral *substance*, $C_{27}H_{46}O_3$, m. p. 236°, which does not react with hydroxylamine or phenylhydrazine, yields a *diacetate*, $C_{31}H_{50}O_5$, m. p. 187°, and a *dipropionate*, $C_{33}H_{54}O_5$, m. p. 166—167°, and by oxidation with chromic and acetic acids is converted into a *diketo*-compound, $C_{27}H_{42}O_3$, m. p. 253°; this is isomeric with Mauthner and Suida's oxycholestendiol (Abstr., 1897, i, 31), and, like the later, yields oxycholestenone by treatment with dehydrating agents. This behaviour indicates that the substance, $C_{27}H_{46}O_3$, contains three hydroxyl groups; a possible formula is suggested.

C. S.

Unsaturated Compounds. IV. Action of Hydroxylamine on Ethyl Cinnamate. Theodor Posner (*Ber.*, 1907, **40**, 218—230. Compare Abstr., 1904, i, 160; 1905, i, 279; 1906, i, 955; Ley, Abstr., 1898, i, 657; Tingle, Abstr., 1900, i, 544; 1905, i, 930).—The action of hydroxylamine on methyl or ethyl cinnamate in cooled methyl-alcoholic solution is much more complicated than that on cinnamic acid, and leads to the formation of *β-hydroxylaminodihydrocinnamhydroxamoxime hydrate*, $OH{\cdot}NH{\cdot}CHPh{\cdot}CH_2{\cdot}C(NH{\cdot}OH)_2{\cdot}OH$, which when purified by solution in aqueous ammonia and reprecipitation by evaporation of the ammonia at the ordinary temperature, is obtained as a white, crystalline powder, m. p. 118—119°, or after some days in a vacuum desiccator, 126° (decomp.), and has strong basic but only feeble acid properties; it gives white *precipitates* with lead acetate and mercuric chloride, and with copper sulphate a blue *precipitate*, which on treatment with hydrogen sulphide yields chiefly β-aminodihydrocinnamic acid together with a yellow, sparingly soluble *substance*, m. p. 174°, containing only 4·9% of nitrogen. In aqueous solution in contact with air at the ordinary temperature, the hydroxamoxime hydrate is converted partially into 3-phenyl*iso*oxazolone, whereas when boiled with ammonia in an open dish on the water-bath it yields β-hydroxylaminodihydrocinnamic acid and only traces of 3-phenyl*iso*oxazolone. The hydroxamoxime hydrate is converted by boiling water into β-aminodihydrocinnamic acid obtained in a 52% yield, or by alcoholic hydrogen chloride at 0° into β-ethoxylaminodihydrocinnamic acid, or by the action of sodium nitrite in cooled dilute sulphuric acid solution into β-dihydroxydihydrocinnamic acid.

The action of benzoyl chloride on the hydroxamoxime hydrate in pyridine solution leads to the formation of three products: (*a*) dibenzhydroxamic acid; (*b*) *dibenzoyl-β-hydroxylaminodihydrocinnamhydroxamic acid*, $OBz{\cdot}NH{\cdot}CHPh{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}OBz$ or

$$OBz{\cdot}NBz{\cdot}CHPh{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}OH,$$

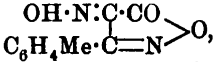
m. p. 136—137°, which crystallises from alcohol, and (*c*) a *hexa-*

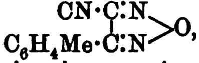
benzoyl derivative, $OBz\cdot NBz\cdot CHPh\cdot CH_2\cdot C(NBz\cdot OBz)_2\cdot OH$, which crystallises from methyl alcohol in needles, m. p. 100—101°. G. Y.

Resin Acids from Conifers. VI. ALBERT VESTERBERG (*Ber.*, 1907, **40**, 120—123. Compare Abstr., 1906, i, 92; Mach, *ibid.*, 1893, i, 582; 1895, i, 384).—Titrations of abietic acid with standard alcoholic potassium hydroxide, using phenolphthalein as indicator, agree with the formula $C_{20}H_{30}O_2$ and not with $C_{19}H_{28}O_2$ (compare Levy, Abstr., 1906, i, 870). When oxidised with sodium hypobromite by Diels and Abderhalden's method (Abstr., 1903, i, 819), a small amount of an acid crystallising in needles, m. p. 199°, was obtained, together with a non-crystalline acid.

d-Pimaric acid distils at 282°/15—20 mm., and is not racemised during the process. J. J. S.

Dinitriles and Amyl Nitrite. JARL LUBLIN (*J. pr. Chem.*, 1906, [ii], **74**, 499—531. Compare Abstr., 1904, i, 890; Meyer, Abstr., 1895, i, 582; Euler, Abstr., 1903, i, 298; Euler and Euler, Abstr., 1904, i, 146).—When amyl nitrite is added in excess to *p*-toluacetodinitrile in ethereal solution, a blue coloration and a dark blue to red, sometimes white, precipitate are formed; when boiled for twenty-four hours, the mixture yields (*a*) the *ammonium* salt of α-*iso*nitroso-β-nitrosoimino-*p*-tolupropionitrile, $NO\cdot N:C(C_7H_7)\cdot C(CN)\cdot NONH_4$, which crystallises in white needles, m. p. 156° (decomp.), detonates when heated, evolves ammonia with aqueous alkalis, and gives a transient blue coloration with acids; the *silver*, $C_{10}H_7O_2N_4Ag$, and *barium*, $(C_{10}H_7O_2N_4)_2Ba$, salts of the *iso*nitrosonitrosoiminonitrile were analysed; and (*b*) the *oxime*, $C_6H_4Me\cdot CO\cdot C(CN):NOH$, which is formed also by the action of heat, mineral acids, or acetic acid on the preceding ammonium salt, or of nitrous acid on benzoylacetonitrile. This separates from benzene in small, slightly yellow crystals, m. p. 130·5—131°, and is hydrolysed only slowly by boiling aqueous sodium hydroxide.

The action of hydroxylamine hydrochloride on the oxime in dilute alcoholic solution leads to the formation of iso*nitroso*-p-*tolyl*iso*oxazolone*,  $\begin{array}{l}OH\cdot N:C\cdot CO\\ C_6H_4Me\cdot C{=}N\end{array}\!>O$, which crystallises in lemon-yellow needles, m. p. 135·5° (decomp.), gives with sodium carbonate solution a stable, with aqueous sodium hydroxide a transient, red coloration, being converted into a *substance* crystallising in white needles, m. p. about 95° (decomp.).

When treated with hydroxylamine hydrochloride and sodium carbonate in aqueous alcoholic solution, the oxime yields a *product* which forms white crystals, m. p. 172°, and may have the constitution  $\begin{array}{l}CN\cdot C:N\\ C_6H_4Me\cdot C:N\end{array}\!>O$, whilst if an excess of hydroxylamine is employed in the reaction the *product* forms white crystals, m. p. 101—102° (decomp.), and is probably the *dioxime*,

$$C_6H_4Me\cdot C(NOH)\cdot C(NOH)\cdot CN;$$

it gives with ferric chloride a red, with hydrogen chloride or amyl nitrite in ethereal solution a blue, coloration, and slowly changes into the preceding substance, m. p. 172°.

The ammonium salt of a-*iso*nitroso-β-nitrosoiminophenylpropionitrile, $C_9H_9O_2N_5$, prepared together with *iso*nitrosocyanoacetophenone by the action of amyl nitrite on benzacetodinitrile, crystallises in white leaflets, m. p. 152—152·5° (decomp.), detonates when heated, and is identical with the product of the interaction of nitrous acid and benzacetodinitrile (Meyer, *loc. cit.*). The action of hydroxylamine hydrochloride on the oxime leads to the formation of *iso*nitrosophenyloxazolone and ammonia.

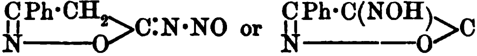
The *ammonium* salt of a-*iso*nitroso-β-nitrosoiminobutyronitrile, formed from amyl nitrite and diacetonitrile, crystallises in white needles or leaflets, m. p. 122°; an oxime corresponding with *iso*nitrosocyanoacetophenone could not be isolated.

p-Tolupropionitrile, acetopropionitrile, and Haller's imino-ether, $CH_2Bz\cdot C(OEt){:}NH$ (Abstr., 1887, 826), do not react with amyl nitrite in ethereal solution.

The *oxime*, $C_6H_4Me\cdot C(NOH)\cdot CH_2\cdot CN$, prepared by Probst's method (*Diss., Leipzig*, 1894), m. p. 150—151°, is converted by hydrogen chloride in ethereal solution into a chlorinated *substance*, which evolves ammonia when boiled with aqueous sodium hydroxide, and with ethereal amyl nitrite yields a blue solution, and on evaporation a small amount of a *product*, m. p. about 205°.

The crystalline substance, m. p. 105—108° (96°, Burns, Abstr., 1893, i, 314), formed by the action of hydroxylamine hydrochloride on diacetonitrile, evolves ammonia when treated successively with hydrogen chloride in ethereal solution and aqueous sodium hydroxide.

The action of ethereal amyl nitrite on phenyl*iso*oxazoloneimide (Obrégia, Abstr., 1892, 324) and treatment of the product with aqueous sodium hydroxide leads to the formation of a red substance,



$$\begin{matrix}CPh\cdot CH_2\\ \|\\ N\text{———}O\end{matrix}\!\!>C{:}N\cdot NO \quad\text{or}\quad \begin{matrix}CPh\cdot C(NOH)\\ \|\\ N\text{————}O\end{matrix}\!\!>C{:}NH$$

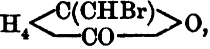
m. p. 63° (decomp.), which forms a resin when evaporated with ether. G. Y.

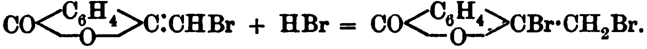
[Dinitriles and Amyl Nitrite.] ERNST VON MEYER (*J. pr. Chem.*, 1906, [ii], **74**, 532. Compare preceding abstract).—The product of the action of hydroxylamine on toluacetodinitrile (Probst, *Diss., Leipzig*, 1894), m. p. 151°, is hydrolysed by alcoholic hydrogen chloride, forming *p*-tolyl cyanomethyl ketone, m. p. 106°, hydroxylamine, and traces of ammonia. The statements of Burns on the formation of an oxime from diacetonitrile (Abstr., 1893, i, 314) are confirmed.

G. Y.

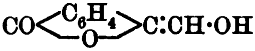
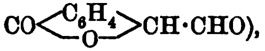
Acetophenone-*o*-carboxylic Acid. SIEGMUND GABRIEL (*Ber.*, 1907, **40**, 71—83).—Gabriel and Michael found (Abstr., 1878, 229) that, when acetophenone-*o*-carboxylic acid (1 mol.) is acted on by bromine in glacial acetic acid solution at 100°, the monobromo-derivative, $CO_2H\cdot C_6H_4\cdot CO\cdot CH_2Br$, was not obtained, but the compound, $C_9H_5BrO_2$, containing 1 mol. of water less than the monobromo-derivative, and having the property of uniting with 1 mol. of bromine, was formed. Gabriel showed subsequently (Abstr., 1884, 1176) that the latter compound was bromomethylenephthalide. The author has now continued the study of the action in question.

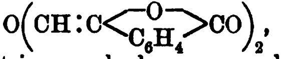
ω-*Bromoacetophenone-o-carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot CH_2Br$, prepared by the addition of bromine to a solution of acetophenone-*o*-carboxylic acid in glacial acetic acid on a water-bath and then evaporating the product under diminished pressure at about 60°, separates from chloroform in snow-white, glassy needles or oblong plates, m. p. 127—128°. Its *methyl ester* crystallises in prisms, m. p. 61—62°.

When heated with a solution of hydrogen bromide in glacial acetic acid for one hour at 100° in a sealed tube, ω-bromoacetophenone-*o*-carboxylic acid forms bromomethylenephthalide (*loc. cit.*), according to the equation $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Br - H_2O =$  $C_6H_4\langle\substack{C(CHBr)\\CO}\rangle O$, if the solution is evaporated on the water-bath. If, however, the solution is allowed to evaporate spontaneously, methylenephthalide dibromide (*loc. cit.*) is formed according to the equation,



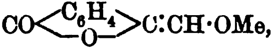
$$CO\langle\substack{C_6H_4\\O}\rangle C{:}CHBr + HBr = CO\langle\substack{C_6H_4\\O}\rangle CBr{\cdot}CH_2Br.$$

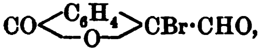
Hydroxymethylenephthalide,  $CO\langle\substack{C_6H_4\\O}\rangle C{:}CH{\cdot}OH$ (or *formylphthalide,*  $CO\langle\substack{C_6H_4\\O}\rangle CH{\cdot}CHO$), is obtained as snow-white needles, m. p. 147—148°, when ω-bromoacetophenone-*o*-carboxylic acid is boiled with water and the solution is allowed to evaporate spontaneously; it is identical with the compound, $C_9H_6O_3$, already described by Michael and Gabriel (*loc. cit.*). It forms a yellow solution with alkalis and reduces Fehling's solution in the cold. By the action of a mixture of fuming hydriodic acid and a little phosphonium iodide, it forms the *compound,* $C_{18}H_{10}O_5$, having the probable formula,

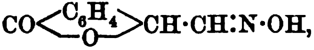


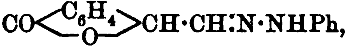
$$O\left(CH{:}C\langle\substack{O\\C_6H_4}\rangle CO\right)_2,$$

m. p. 240° (decomp.); it is an anhydro-compound, being formed according to the equation, $2C_9H_6O_3 - H_2O = C_{18}H_{10}O_5$.

The presence of a hydroxy-group in hydroxymethylenephthalide is also indicated by its behaviour on esterification with methyl alcohol according to the hydrogen chloride method, when *methoxymethylenephthalide,*  $CO\langle\substack{C_6H_4\\O}\rangle C{:}CH{\cdot}OMe$, is produced; the latter separates from alcohol in needles, m. p. 75°.

That a double linking is present in the molecule of hydroxymethylenephthalide is attested by its behaviour on bromination. When acted on by bromine in chloroform solution, it forms *formylbromophthalide,*  $CO\langle\substack{C_6H_4\\O}\rangle CBr{\cdot}CHO$, which separates from alcohol in hexagonal plates, m. p. 85—86°.

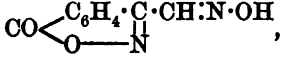
In certain reactions, however, hydroxymethylenephthalide behaves as if it were an aldehyde. For example, it forms an *oxime,*  $CO\langle\substack{C_6H_4\\O}\rangle CH{\cdot}CH{:}N{\cdot}OH$, which crystallises in silky needles, m. p. 147—152°, the *acetyl* derivative of which has m. p. 154—155°.

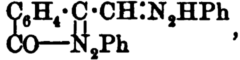
The *phenylhydrazone,*  $CO\langle\substack{C_6H_4\\O}\rangle CH{\cdot}CH{:}N{\cdot}NHPh$, obtained from hydroxymethylenephthalide and phenylhydrazine, forms yellow needles, m. p. 180°.

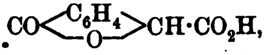
Similarly, hydrazine hydrate forms the *azine*, $C_{18}H_{12}O_4N_2$, which crystallises in yellow needles, and begins to decompose at about 220°.

The *compound*, $C_{19}H_{13}O_6N$, obtained by the action of potassium cyanide on ω-bromoacetophenone-*o*-carboxylic acid, forms a brown powder, m. p. 223°. It reduces Fehling's solution in the cold.

ω-Dibromoacetophenone-o-carboxylic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot CHBr_2$, prepared by the action of bromine (2 mols.) on a solution of acetophenone-*o*-carboxylic acid in glacial acetic acid, separates from chloroform in tetragonal, colourless plates, m. p. 131—132°. Its *methyl ester* separates from alcohol in hexagonal plates or oblong prisms, m. p. 112°.

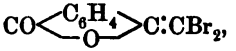
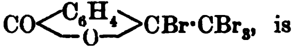
By the action of hydroxylamine on ω-dibromoacetophenone-*o*-carboxylic acid, both the halogen and the ketonic oxygen of the latter are replaced, with the formation of *phthalonaldehydecarboxylic acid dioxime anhydride*,  $CO{<}\begin{array}{l}C_6H_4\cdot C\cdot CH{:}N\cdot OH\\ O\text{———}N\end{array}$, which crystallises from glacial acetic acid in silky needles, m. p. 163°.

The behaviour of ω-dibromoacetophenone-*o*-carboxylic acid towards phenylhydrazine is analogous, *phthalonaldehydecarboxylic acid osazone anhydride*,  $\begin{array}{l}C_6H_4\cdot C\cdot CH{:}N_2HPh\\ CO\text{—}N_2Ph\end{array}$, being formed; the latter compound separates from glacial acetic acid in silky needles, m. p. 228°.

When ω-dibromoacetophenone-*o*-carboxylic acid is boiled with water, it is converted into phthalidecarboxylic acid,  $CO{<}\begin{array}{c}C_6H_4\\O\end{array}{>}CH\cdot CO_2H$, melting at 152° and identical with the product obtained by Zincke and Schmidt. In this action, phthalonaldehydic acid,

$$CO_2H\cdot C_6H_4\cdot CO\cdot CHO,$$

was possibly first formed and then underwent molecular rearrangement into its isomeride.

Dibromomethylenephthalide,  $CO{<}\begin{array}{c}C_6H_4\\O\end{array}{>}C{:}CBr_2$, obtained by the action of concentrated sulphuric acid on ω-dibromoacetophenone-*o*-carboxylic acid, separates from alcohol in needles, m. p. 139—140°. Its unsaturated nature is demonstrated by its behaviour towards bromine, when *tetrabromomethylphthalide*,  $CO{<}\begin{array}{c}C_6H_4\\O\end{array}{>}CBr\cdot CBr_3$, is produced; the latter separates from a mixture of benzene and ethyl acetate in glistening pyramids which melt and decompose at 160—161°.

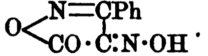
A. McK.

Catecholcarboxylic Acids. ANTON PRAXMARER (*Monatsh.*, 1906, **27**, 1199—1209).—Contrary to Miller's statement (*Annalen*, 1883, **220**, 113), the action of ammonium carbonate on catechol at 130—140° under pressure leads to the formation of catecholcarboxylic acid only; protocatechuic acid cannot be found in the product. The same result is obtained on heating catechol with glycerol and potassium hydrogen carbonate in a current of carbon dioxide at 180° for twelve to sixteen hours, or at 210° for six to eight hours.

Catecholcarboxylic acid, $C_7H_6O_4,\frac{1}{2}H_2O$, m. p. 240°, decomposes, evolving carbon dioxide a few degrees above its melting point. The barium, $(C_7H_5O_4)_2Ba,4H_2O$ ($5H_2O$, Miller, *loc. cit.*), and calcium ($2\frac{1}{2}H_2O$) salts and the ethyl ester, m. p. 130·5° (63—64°, Schmitt and Hähle, Abstr., 1891, 1366), are described. The methyl ester of the dimethyl ether, m. p. 57·5° (47°, Fritsch, Abstr., 1898, i, 663), is prepared by the action of methyl iodide and potassium hydroxide on the acid in methyl alcoholic solution. The action of bromine on catecholcarboxylic acid in absence of a solvent leads to the formation of tetrabromocatechol, or in ethereal solution to the formation of this together with *dibromocatecholcarboxylic acid*, $C_7H_4O_4Br_2$, which is soluble in water at 80°.

Catecholdicarboxylic acid is formed together with a small amount of catechol by heating the monocarboxylic acid with glycerol, potassium hydrogen carbonate, and a little sodium sulphite in a current of carbon dioxide at 210° for six hours. A product which gives the green coloration of protocatechuic acid with ferric chloride is obtained on heating catechol with sodium hydrogen carbonate and glycerol at a temperature not above 139°. G. Y.

Ethyl Benzoylglyoxylate. ANDRÉ WAHL (*Compt. rend.*, 1907, **144**, 212—214. Compare Abstr., 1904, i, 556).—*Ethyl benzoylglyoxylate*, $COPh\cdot CO\cdot CO_2Et$, prepared by passing nitrous anhydride into a mixture of ethyl benzoylacetate and acetic anhydride dissolved in ether, is an orange-yellow liquid, mobile when freshly prepared and without distinctive odour, b. p. 150—153°/13 mm.; D_0^0 1·188. It combines with water and alcohol developing much heat, and forming colourless hydrates and alcoholates which do not crystallise. By adding a few drops of piperidine to a molecular mixture of ethyl benzoylglyoxylate and ethyl benzoylacetate, the author has obtained a compound, $C_{11}H_{12}O_3,C_{11}H_{10}O_4$, forming white needles, m. p. 109—110°, and probably identical with that obtained by Sachs and Wolff (Abstr., 1904, i, 876), and having m. p. 91·5°. Ethyl benzoylglyoxylate forms a *monoxime* identical with ethyl *iso*nitrosobenzoylacetate and hence having the constitution $COPh\cdot C(:NOH)\cdot CO_2Et$; a dioxime is not formed. Crismer's method gave a small quantity of a crystalline substance which showed the reaction of oximinophenyl*iso*oxazolone,



The ester reacts with *o*-phenylenediamine, forming *ethyl 2-phenylquinoxaline-3-carboxylate*, which crystallises in slender, white needles, m. p. 65—66°. It gives a *disemicarbazone*, $C_{18}H_{16}O_4N_6,H_2O$, light yellow needles, m. p. 185—190°, and a *dianilide*, $C_{23}H_{22}O_3N_2$, small, yellow needles, m. p. 127°. E. H.

Condensation Products of Dibromophthalic Acid. ÉMILE SÉVERIN (*Ann. Sci. Univ. Jassy*, 1907, **4**, 141—150).—Most of the work recorded in this paper has been published already (Abstr., 1906, i, 508). 3 : 6-Dibromo-2-*o*-diethylaminobenzoylbenzoic acid,

$$NEt_2\cdot C_6H_4\cdot CO\cdot C_6H_2Br_2\cdot CO_2H,$$

prepared as already described (*loc. cit.*), furnishes an *ethyl ester*, m. p. 145°, which crystallises with alcohol; the *nitroso*-derivative,

$$NO\cdot NEt_2\cdot C_6H_3\cdot CO\cdot C_6H_2Br_2\cdot CO_2H,$$

m. p. 155°, crystallises in yellow needles. On reduction of the benzoylbenzoic acid, the corresponding *dibromodiethylaminobenzylbenzoic acid* is produced, which separates from alcohol with difficulty in colourless needles, m. p. 247°, and when warmed with sulphuric acid at 66° furnishes 1-*diethylamino*-5 : 8-*dibromoanthraquinone*, which sublimes in red needles, m. p. 198°. T. A. H.

Behaviour of Phenolphthalein towards Highly Concentrated Alkali Hydroxides. BENJAMIN M. MARGOSCHES (*Zeitsch. angew. Chem.*, 1907, **20**, 181—191 and 226—231).—Alkaline solutions containing phenolphthalein may be decolorised by the addition of very concentrated solutions of alkali hydroxides, and to a less extent by the addition of lithium hydroxide. Such solutions recover their pink colour on warming or on dilution; as the colour is, however, not instantaneously restored by dilution, the phenomenon cannot be completely explained by dissociation. The paper contains a very full account of the various theories which have been put forward with regard to the constitution of phenolphthalein and its use as an indicator. P. H.

Compounds from Lichens. XVI. WILHELM ZOPF (*Annalen*, 1907, **352**, 1—44. Compare Abstr., 1906, i, 672).—The lichen, *Ramalina subfarinacea*, contains *d*-usnic acid, $[\alpha]_D^{17}$ +492·5°, to the extent of $\frac{1}{3}$% and 3 to $3\frac{1}{2}$% of salazinic acid; the product obtained by the action of acetic anhydride on the latter acid has already been described as salazinaric acid (Zopf, Abstr., 1905, i, 789), but is now thought to be the *acetyl* derivative of salazinic acid, $C_{21}H_{16}O_{11}$; its mol. weight was determined cryoscopically in benzene and found to be 455, Hesse's formula for salazinic acid, $C_{30}H_{24}O_{16}$ (Abstr., 1901, i, 595), cannot therefore be correct.

In addition to *d*-usnic acid ($[\alpha]_D^{18}$ +495·5°), *Ramalina scopulorum* is found to contain a new acid, *scopuloric acid*, $C_{19}H_{16}O_9$, which crystallises in white needles, m. p. 260° (decomp.). The *acetyl* derivative, $C_{21}H_{18}O_{10}$, crystallises in white needles, m. p. 235—236°. *Ramalina Kullensis* contains about 0·1% of *d*-usnic acid, $[\alpha]_D^{22}$ +461·9°, and 2% of *kullensisic acid*, $C_{22}H_{18}O_{12}$, a substance not yet met with in any other lichen; it crystallises in white needles and carbonises at 260°.

Only *d*-usnic acid was obtained from *Ramalina minuscula*, whilst *R. Landroënsis* contains in addition to about 0·5% of *d*-usnic acid about 0·1% of *landroënsin*, which crystallises from benzene in small, rhombic plates.

The lichen, *Ramalina obtusata* (*R. minuscula* var. *obtusata*, *R. dilacerata* var. *obtusata*), contains only small quantities of *d*-usnic acid, $[\alpha]_D^{22}$ +474·2°, together with two new acids. *Ramalinellic acid* crystallises from acetone in small needles, m. p. 169°. *Obtusatic acid* crystallises in needles, m. p. 191°.

Cladonia fimbriata var. *simplex*, obtained from Daun in Eifel, was found to differ from a *Cladonia fimbriata* var. *simplex*, obtained from the Dortmund-Ems Canal near Münster i. W., in that the first contained fumaroprotocetraric acid together with fimbriatic acid, whereas the latter lichen, besides these two acids also contained atranoric acid; it is therefore probable that they are specifically different. *Fimbriatic acid* crystallises from ether in leaflets, m. p. 98—99°; it reduces potassium permanganate immediately in alkaline solution. The lichen, *Cladonia fimbriata* var. *cornuto-radiata*, contains only fumaroprotocetraric acid. Hesse obtained from this lichen, called wrongly by him *C. fimbriata* var. *chordalis* (compare Abstr., 1901, i, 149), protocetraric acid and not fumaroprotocetraric acid, probably because he employed sodium hydrogen carbonate to extract the acids from the lichen, and thus decomposed the fumaroprotocetraric acid into fumaric and protocetraric acids. Closely related to this latter lichen is *Cladonia pityrea* var. *cladomorpha*, since this also contains only fumaroprotocetraric acid. *Cladonia squamosa* var. *denticollis* contains squamatic acid, but not usnic acid.

Cladonia silvatica var. *condensata*, besides *l*-usnic acid, $[\alpha]_D^{22}$ − 499·5°, contains a *substance* which, since it is relatively soluble in cold benzene and ether, is not fumaroprotocetraric acid; as the latter acid together with *d*-usnic acid is present in the typical *C. silvatica* (Zopf, Abstr., 1906, i, 673), *C. silvatica* var. *condensata* cannot be regarded as a variety of *C. silvatica*, but must either be regarded as a variety of *C. alpestris* or, better, be named simply *C. condensata*.

Cladonia verticillata var. *subcervicornis* contains about 1% of fumaroprotocetraric acid and a small quantity of atranoric acid; there is also present a small amount of a red pigment, *cervicornin*, a red, amorphous substance coloured blue by strong sulphuric acid, and violet to violet-brown by potassium and sodium hydroxides.

Cladonia chlorophæa contains fumaroprotocetraric acid together with *chlorophæaic acid*, which crystallises in leaflets, m. p. 169° (decomp.).

Cladonia gracilis var. *chordalis* contains only fumaroprotocetraric acid; *C. crispata* var. *gracilescens* contains only squamatic acid. The same acid is also present in *C. squamosa* var. *multibrachiata* f. *pseudocrispata* and *C. squamosa* var. *multibrachiata* f. *turfacea*.

Hypogymnia farinacea contains about 0·5% of atranoric acid together with about 4·5% of *farinacinic acid*, $C_{26}H_{32}O_8$; this acid crystallises in white needles, m. p. 202—203°; its mol. weight was determined in acetone; it does not taste bitter. When heated with acetic anhydride, a *substance*, m. p. 156—157°, is obtained. It is possible that this acid is identical with Hesse's physodic acid (Abstr., 1898, i, 679).

W. H. G.

Derivatives of Methylvanillin [2:4-Dimethoxybenzaldehyde].

FRITZ JULIUSBERG (*Ber.*, 1907, **40**, 119—120).—2:4-Dimethoxybenzaldehyde, obtained by methylating vanillin by means of sodium ethoxide and methyl iodide, has m. p. 47°. 2:4-*Dimethoxybenzaldehydephenylhydrazone*, $C_6H_3(OMe)_2\cdot CH\colon N\cdot NHPh$, has m. p. 121°.

1:2-*Dimethoxy-4-benzaldoxime*, $C_6H_3(OMe)_2\cdot CH\colon N\cdot OH$, obtained by the action of hydroxylamine on the aldehyde, softens at 87° and has m. p. 90°.

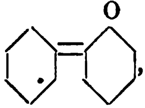
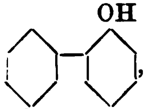
1:2-*Dimethoxy-4-benzylamine hydrochloride*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot NH_2,HCl,$$

obtained by the reduction of the preceding oxime with sodium amalgam and acetic acid, has m. p. 257—258°. A. McK.

Influence of Cyclic Linking on Reactivity. Pavel Petrenko-Kritschenko (*J. pr. Chem.*, 1907, [ii], **75**, 61—64. Compare Abstr., 1900, i, 421; 1901, i, 506; 1903, i, 440; *ibid.*, ii, 719; 1905, i, 355, 742; 1906, ii, 341).—The author replies to Stewart and Baly (Trans., 1906, **89**, 489) that the relations which he has observed (*loc. cit.*) to exist between the velocity of reaction and the structure of ketones are completely analogous to those found by Menschutkin in the case of aliphatic and aromatic alcohols and amines in which all possibility of tautomerism is excluded.

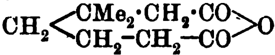
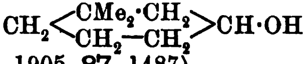
The author compares his theoretical views which have been described previously (*loc. cit.*) with those of Menschutkin (Trans., 1906, **89**, 1532). G. Y.

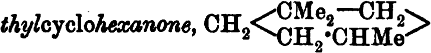
Condensation Products from *cyclo*Hexanone. Otto Wallach (*Ber.*, 1907, **40**, 70—71. Compare Abstr., 1906, i, 514).—The *chloride*, $C_{12}H_{19}OCl$, obtained by passing a current of dry hydrogen chloride into *cyclo*hexanone, forms colourless crystals, m. p. 41—43°. On rise of temperature, it loses hydrogen chloride and forms cyclo*hexene*-2-cyclo*hexanone*, , which, on reduction, forms the saturated alcohol, cyclo*hexyl*-2-cyclo*hexanol*, , b. p. 265—270°, m. p. 30—31°. The latter compound, when warmed with hydriodic acid, forms the completely hydrogenated diphenyl, di*cyclo*hexyl, $C_6H_{11}\cdot C_6H_{11}$, already described by Borsche and Lange (Abstr., 1905, i, 765).

*Benzylidene*cyclo*hexanone*, $C_6H_4O:CHPh$, has m. p. 53°. *Dibenzylidene*cyclo*hexanone*, $C_{13}H_{14}O$, has m. p. 116—118°.

By the action of hydroxylamine on monobenzylidene*cyclo*hexanone, a *compound* of m. p. 104°, crystallising in needles, is obtained.

A. McK.

Synthesis of Derivatives of *cyclo*Hexane. 3:3-Dimethyl- and 3:3:6-Trimethyl-*cyclo*hexanones. Gustav Blanc (*Compt. rend.*, 1907, **144**, 143—144. Compare Abstr., 1906, i, 399).—The anhydride,  $CH_2<\begin{matrix}CMe_2\cdot CH_2\cdot CO\\ CH_2-CH_2-CO\end{matrix}>O$, obtained from $\beta\beta$-dimethylpimelic acid by the action of acetic anhydride, loses carbon dioxide on slow distillation at the ordinary pressure, and gives the 3:3-dimethyl*cyclo*hexanone already described by Léser (Abstr., 1899, i, 743). This compound forms a semicarbazone crystallising in needles, m. p. 203° (Léser gives 198°). On reduction by means of sodium and absolute alcohol it gives the alcohol,  $CH_2<\begin{matrix}CMe_2\cdot CH_2\\ CH_2-CH_2\end{matrix}>CH\cdot OH$, obtained by Crossley and Renouf (Trans., 1905, **87**, 1487).



Similarly, slow distillation of $\beta\beta\epsilon$-trimethylpimelic anhydride gives 3:3:6-*trimethyl*cyclo*hexanone*, $CH_2<\begin{matrix}CMe_2-CH_2\\CH_2\cdot CHMe\end{matrix}>CO$, a mobile liquid, b. p. 186°, of strong menthone-like odour. The *semicarbazone* has m. p. 170°. E. H.

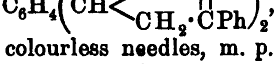
Change of 2-*iso*Nitroso-1-ketohydrindene into Homophthalamic Acid. WALTER PETERS (*Ber.*, 1907, **40**, 240—241).—The oxime is unchanged by cold hydrochloric and acetic acids, is oxidised to phthalic acid by nitric acid, and is converted by concentrated sulphuric acid at 0° into Gabriel's homophthalamic acid (Abstr., 1887, 726). C. S.

Condensation of Cinnamyl Chloride with *o*-Cresol. GUSTAV NEURATH (*Monatsh.*, 1906, **27**, 1145—1156. Compare Feuerstein and Kostanecki, Abstr., 1898, i, 370; Kostanecki and Tambor, Abstr., 1899, i, 704).—p-*Hydroxy*-m-*tolyl styryl ketone* (*4'-hydroxy-3'-methylchalkone*), $OH\cdot C_6H_3Me\cdot CO\cdot CH:CHPh$, prepared by the action of cinnamyl chloride and aluminium chloride on *o*-cresol in nitrobenzene solution, or by heating *o*-cresol with cinnamic acid and zinc chloride at 200°, crystallises from water in reddish-yellow, nacreous needles, m. p. 137° (corr.), and is soluble in aqueous alkalis.

The *acetyl* derivative, $C_{18}H_{16}O_3$, crystallises in needles, m. p. 72° (corr.); the *oxime*, $C_{16}H_{15}O_2N$, forms a ruby-red, crystalline mass, m. p. 49° (corr.). The *dibromide*, $OH\cdot C_6H_3Me\cdot CO\cdot CHBr\cdot CHPhBr$, formed by the action of bromine on the unsaturated ketone in ethereal solution, separates in yellowish-red crystals, m. p. 135° (corr.). G. Y.

Condensation of Terephthalaldehyde with Ketones. HANS VON LENDENFELD (*Monatsh.*, 1906, **27**, 969—980. Compare Thiele and Winter, Abstr., 1900, i, 500; Thiele and Günther, and Thiele and Falk, Abstr., 1906, i, 750).—The condensation of terephthalaldehyde with ketones in hot alcoholic potassium hydroxide solution leads to the formation of unsaturated ketones, or, in cooled glacial acetic acid solution in presence of hydrogen chloride, to that of the corresponding hydrogen chloride additive products. Aldols are not formed.

Terephthalaldehyde and acetophenone yield a mixture of p-*aldehydobenzylideneacetophenone*, $COH\cdot C_6H_4\cdot CH:CH\cdot COPh$, which crystallises from methyl alcohol in slightly yellow needles, m. p. 125°, and forms a yellow solution in concentrated sulphuric acid, and *terephthalylidenediacetophenone*, $C_6H_4[CH:CH\cdot COPh]_2$, which crystallises from chloroform in yellow, hexagonal plates, m. p. 200—201°, and is insoluble in methyl alcohol. With phenylhydrazine the latter substance forms p-*phenylenebis*-1:3-*diphenyl*-4:5-*dihydropyrazole*,



$$C_6H_4\left(CH<\begin{matrix}NPh\cdot N\\ \qquad\| \\CH_2\cdot CPh\end{matrix}\right)_2,$$

which crystallises in colourless needles, m. p. 300° (slight decomp.), and gives Knorr's pyrazoline reaction.

The *additive* product, $C_6H_4[CHCl\cdot CH_2\cdot COPh]_2$, crystallises from nitrobenzene in colourless needles, m. p. 194—195°, and at 160—170°

gradually decomposes, yielding terephthalylidenediacetophenone and hydrogen chloride.

The *condensation product* of terephthalaldehyde with phenyl ethyl ketone, $C_6H_4[CH\colon CMe\cdot COPh]_2$, crystallises from alcohol in colourless, hexagonal leaflets, m. p. 162°, and reacts with phenylhydrazine, forming a *product* which crystallises from pyridine in yellow needles, sinters at 245°, and is decomposed to a clear liquid at 254°. The hydrogen chloride *additive* product, $C_6H_4[CHCl\cdot CHMe\cdot COPh]_2$, crystallises from benzene in long, rhombic plates, decomposing at 240° yielding the unsaturated ketone.

p-*Tolyl* p-*aldehydobenzylidenemethyl ketone*,

$$COH\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot C_7H_7,$$

formed from a molecular mixture of terephthalaldehyde and *p*-tolyl methyl ketone, crystallises in small, matted, yellow needles, m. p. 130°. The *phenylhydrazone*, $C_{23}H_{20}ON_2$, forms red needles, m. p. about 224°.

The *diketone*, $C_6H_4[CH\colon CH\cdot CO\cdot C_7H_7]_2$, formed from 1 mol. of terephthalaldehyde and 2 mols. of *p*-tolyl methyl ketone, crystallises from alcohol in needles, m. p. 236—238°, gives an orange-red coloration with concentrated sulphuric acid, and reacts with phenylhydrazine in glacial acetic acid solution, forming an amorphous product which gives the pyrazoline reaction. The hydrogen chloride *additive* product, $C_6H_4[CHCl\cdot CH_2\cdot CO\cdot C_7H_7]_2$, crystallises in colourless needles, m. p. 228—230°, and yields the unsaturated diketone when heated in a vacuum at 170°.

p-*Methoxyphenol* p-*aldehydobenzylidenemethyl ketone*,

$$COH\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot C_6H_4\cdot OMe,$$

obtained by the interaction of terephthalaldehyde and anisyl methyl ketone in molecular proportions, crystallises in large, yellow needles, m. p. 121°; the *phenylhydrazone*, $C_{23}H_{20}O_2N_2$, crystallises in reddish-yellow needles, m. p. 208° (decomp.).

The *diketone*, $C_6H_4[CH\colon CH\cdot CO\cdot C_6H_4\cdot OMe]_2$, forms large, yellow leaflets, m. p. 250°, and gives a red coloration with concentrated sulphuric acid. The product formed by the action of hydrogen chloride on terephthalaldehyde and anisyl methyl ketone in glacial acetic acid solution is identical with that obtained by the condensation in presence of alcoholic potassium hydroxide. G. Y.

Halogen Derivatives of 1 : 3 : 4-Triketo*cyclo*pentane. III.

FRANZ HENLE (*Annalen*, 1907, **352**, 45—53. Compare Abstr., 1907, i, 144, 161).—Tetrahalogen derivatives of 1 : 3 : 4-triketo*cyclo*pentane cannot be prepared by the direct bromination or chlorination of chlorotriketo*cyclo*pentane; they are, however, obtained by acting on either tribromotriketo*cyclo*pentane or chlorodibromotriketo*cyclo*pentane with phosphorus pentachloride; phosphorus pentabromide does not react like phosphorus pentachloride; it replaces a hydroxyl group by bromine, so that from tribromotriketo*cyclo*pentane, tetrabromodiketo*cyclo*pentene is obtained.

Chlorodibromotriketo*cyclo*pentane may be prepared by acting on chloro-1 : 3 : 4-triketo*cyclo*pentane dissolved in thionyl chloride with bromine. When treated with phosphorus pentachloride it gives *trichlorobromo*-1 : 3 : 4-*triketo*cyclo*pentane*, $C_5O_3Cl_3Br$, which crystallises in faintly yellow plates, m. p. 85°.

Tribromo-1 : 3 : 4-triketo*cyclo*pentane is converted by phosphorus pentachloride into *dichlorodibromo*-1 : 3 : 4-*triketo*cyclo*pentane*,

$$C_5O_3Cl_2Br_2,$$

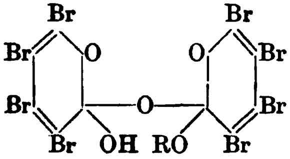
which crystallises in yellow prisms, m. p. 102°. With phosphorus pentabromide, however, *tetrabromo*-1 : 3-*diketo*cyclo*pentene*, $C_5O_2Br_4$, is obtained, which crystallises in yellow needles, m. p. 142°.

By heating dichlorodibromo-1 : 3 : 4-triketo*cyclo*pentane with phosphorus pentachloride in sealed tubes at 280—300°, octachloro*cyclo*pentene, C_5Cl_8, is formed, identical with that described by Zincke (Abstr., 1890, 1256).

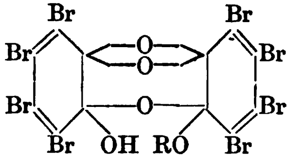
W. H. G.

Constitution of the α- and β-Additive Compounds of Alcohols and Tetrabromo-*o*-benzoquinone. C. LORING JACKSON and ROBERT D. MACLAURIN (*Amer. Chem. J.*, 1907, **37**, 87—106).—Jackson and Porter (Abstr., 1903, i, 266; 1904, i, 254) have described two series of additive compounds, $2C_6Br_4O_2$, R·OH, obtained by the combination of tetrabromo-*o*-benzoquinone with alcohols. The α-compounds are formed by the direct action of alcohols on the quinone at the ordinary temperature, and are converted into the β-compounds by the action of hot dilute sodium hydroxide or by means of acetic anhydride. Further work on these substances has been carried out by Jackson and Carlton (Abstr., 1905, i, 907) and by Jackson and Russe (Abstr., 1906, i, 288).

Further investigation has led to the conclusion that the α- and β-compounds have respectively the constitutions expressed by the following formulæ:



and



The reasons for adopting these formulæ in preference to those previously assigned to these compounds are fully discussed and are based chiefly on the facts that the regulated action of acetic anhydride converts the α-benzyl compound into the β-compound and that the β-compounds are remarkably stable. In accordance with these formulæ, the α- and β-methyl compounds are termed respectively octabromo-1-methoxy-1′-hydroxy-*o*-quino-1-monoxide and octabromo-1-methoxy-1′-hydroxy-*o*-quino-1 : 2 : 2-trioxide.

On adding a considerable quantity of sodium hydroxide solution to hexachloro-*o*-quinocatechol ether, $C_6Cl_4O_2{:}C_6Cl_2O_2$, an additive *compound*, $C_{12}Cl_6O_4$,NaOH, separates in purplish-black, short, stout needles. If, however, sodium hydroxide is added drop by drop to a warm mixture of hexachloro-*o*-quinocatechol and water, hexachlorodihydroxycatechol ether and sodium chloroanilate are produced. It is evident that the former product is formed from the tetrachlorocatechol resulting from the decomposition of the hexachloro-*o*-quinocatechol ether, since on warming tetrachlorocatechol with dilute sodium hydroxide, hexachlorodihydroxycatechol ether is produced.

When hexabromo-*o*-quinocatechol ether is left in contact with dilute sodium hydroxide, sodium bromoanilate is formed.

It has been shown by Jackson and Porter (Abstr., 1904, i, 256) that by the action of heat on tetrabromo-*o*-quinone, bromine is liberated and hexabromo-*o*-quinocatechol ether is produced. It is now found that tetrachloro-*o*-quinone is decomposed similarly by heat with formation of hexachloro-*o*-quinocatechol ether.

The β-methyl compound, $2C_6Br_4O_2,CH_3\cdot OH$, is more stable towards sodium ethoxide than the α-compound, but is gradually decomposed with formation of catechol and sodium bromide. By the action of hydroxylamine on the α-methyl compound, it is converted quantitatively into the β-compound. If the α-methyl compound is shaken with acetic anhydride for fifteen minutes and then left for several hours, an isomeric *γ-compound*, m. p. 225°, is produced, which crystallises in yellow plates and is more soluble in organic solvents than the β-compound. By the action of warm acetic acid on the γ-compound, there are successively produced a white *substance*, m. p. 138—140°, a second *compound*, m. p. 195°, and, finally, hexabromo-*o*-quinocatechol ether. E. G.

Preparation of 1-Aminoanthraquinone and its *N*-Alkyl or Acyl Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 175024).—When heated with aqueous ammonia or methylamine, anthraquinone-α-sulphonic acid is converted respectively into 1-aminoanthraquinone or 1-methylaminoanthraquinone. With *p*-toluidine this sulphonic acid yields 1-*p*-toluidinoanthraquinone.

G. T. M.

Preparation of Arylaminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 175069).—The halogenated benzenes interact readily with the aminoanthraquinones in presence of an acid-fixing agent to form arylaminoanthraquinones. Thus *p*-chloronitrobenzene and 1-aminoanthraquinone yield 1-*p*-nitroanilinoanthraquinone, and 1 : 4-diaminoanthraquinone and *p*-dichlorobenzene give rise to 1 : 4-di-*p*-chloroanilinoanthraquinone. The colour reactions of these and other arylaminoanthraquinones are tabulated. G. T. M.

Preparation of Aldehydes of the Anthraquinone Series. BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 174984).—Although ωω-dichloromethylanthraquinone does not yield an aldehyde on treatment with alkalis or water at high temperatures, yet it undergoes this change on heating with concentrated sulphuric acid either alone or with addition of boric acid.

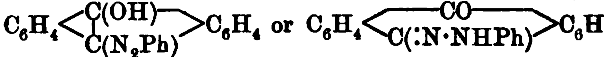
β-Anthraquinonealdehyde is obtained in this way from ω-dichloro-β-methylanthraquinone, or the corresponding bromine compound.

1-*Chloro-β-anthraquinonealdehyde* is produced by the interaction of 1-chloro-2-methylanthraquinone and sulphuric and boric acids at 130°.

4-*Bromo*-1-*hydroxy-β-anthraquinonealdehyde* is prepared in this way from 4-ωω-tribromo-1-hydroxy-2-methylanthraquinone. G. T. M.

Meso-derivatives of Anthracene. Felix Kaufler and W. Suchannek (*Ber.*, 1907, 40, 518—532).—Anthranol and diazobenzene chloride form a substance which may be regarded either as a benzeneazoanthranol from its forming alkali salts, or as an anthraquinonephenylhydrazone from its colour, its ready decomposition into anthraquinone and phenylhydrazine, and its formation from dibromoanthrone and phenylhydrazine. 9-Aminoanthracene reacts with diazonium salts in a similar manner.

10-*Benzeneazoanthranol* (*anthraquinone-β-phenylhydrazone*),

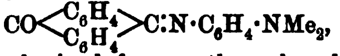


$$C_6H_4\left<\begin{matrix}C(OH)\\C(N_2Ph)\end{matrix}\right>C_6H_4 \text{ or } C_6H_4\left<\begin{matrix}CO\\C(:N\cdot NHPh)\end{matrix}\right>C_6H_4,$$

m. p. 182—183°, is obtained from the potassium salt of anthranol and diazobenzene chloride in alkaline solution, or from 10-dibromoanthrone and phenylhydrazine; it separates from toluene in red needles, forms a potassium salt which exhibits bluish-red fluorescence in solution, and is converted by boiling alcoholic sulphuric acid into anthraquinone and phenylhydrazine.

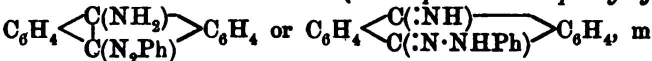
10-p-*Nitrobenzeneazoanthranol*, m. p. 238—240°, is prepared in a similar manner to the preceding compound and exhibits similar properties.

Anthraquinone-10-p-*dimethylaminoanil*,



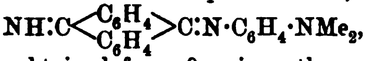
$$CO\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>C:N\cdot C_6H_4\cdot NMe_2,$$

m. p. 138—139°, is obtained from anthranol and p-nitrosodimethylaniline; it separates from light petroleum in bluish-black, glistening needles, and by hydrolysis yields anthraquinone and dimethyl-p-phenylenediamine.

9-*Amino*-10-*benzeneazoanthracene* (*anthraquinoneimidephenylhydrazone*),  $C_6H_4\left<\begin{matrix}C(NH_2)\\C(N_2Ph)\end{matrix}\right>C_6H_4$ or $C_6H_4\left<\begin{matrix}C(:NH)\\C(:N\cdot NHPh)\end{matrix}\right>C_6H_4$, m. p. 182—184°, is obtained in the form of the hydrochloride by the action of diazobenzene chloride on 9-aminoanthracene in cold alcoholic solution; it forms large, brown crystals, and is changed by 3% alcoholic hydrogen chloride into anthraquinone, ammonia, and phenylhydrazine; the *hydrochloride*, $C_{20}H_{15}N_3,HCl$, forms red crystals with green reflex.

9-*Amino*-10-p-*nitrobenzeneazoanthracene*, $C_{20}H_{14}O_2N_4$, m. p. 239—240°, forms yellowish-brown leaflets.

The p-*dimethylaminoanil* of anthraquinoneimide,



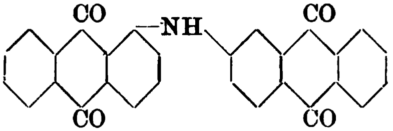
$$NH:C\left<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right>C:N\cdot C_6H_4\cdot NMe_2,$$

m. p. 118—124°, is obtained from 9-aminoanthracene and p-nitrosodimethylaniline in alcoholic solution; it crystallises in black leaflets or prisms, and is converted by 1% acetic acid in alcohol into anthraquinonedimethylaminoanil, and by 1% alcoholic hydrogen chloride into anthraquinone, ammonia, and dimethyl-p-phenylenediamine.

Attempts to diazotise 9-aminoanthracene lead to the formation of anthraquinone and a basic *substance* which appears to be diaminodianthryl, $C_{28}H_{20}N_2$; the best yield is obtained by diazotising with amyl nitrite and sulphuric acid in alcoholic solution. The basic substance is nearly colourless, darkens at 192°, has m. p. 201—202°, yields anthraquinone by oxidation with chromic and acetic acids, and forms well-defined di-acid salts; the *nitrate*, $C_{28}H_{20}N_2,2HNO_3,3H_2O$, forms colourless needles; the *hydrobromide*, $C_{28}H_{20}N_2,2HBr,5H_2O$, forms stout crystals. C. S.

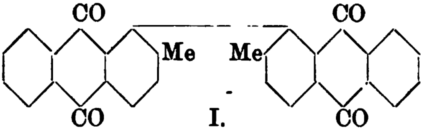
[Dianthraquinonylamine.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 174699).—Halogenated anthraquinones condense with aminoanthraquinones under the influence of metallic salts to form complex secondary amines.

A *dianthraquinonylamine* having the annexed formula is readily prepared by heating together for fifteen hours 2-chloroanthraquinone, 1-aminoanthraquinone, naphthalene, anhydrous sodium acetate, and cupric chloride. The product, which is obtained in well-defined crystals having a metallic lustre, dissolves in concentrated sulphuric acid to a greenish-blue solution, and may be crystallised from aniline or nitrobenzene.

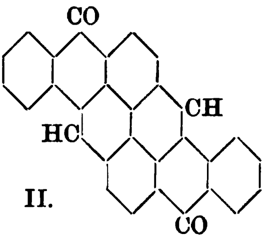


G. T. M.

Preparation of Anthracene Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 175067).—2:2-Dimethyl-1:1′-dianthraquinonyl and its derivatives, which are prepared from 1-chloro-2-methylanthraquinone and its derivatives by the action of copper powder, are now found to undergo a further condensation in the presence of dehydrating agents. The substance represented by the formula I loses $2H_2O$ and becomes converted into the *compound* II, which is insoluble in water, dilute acids, and alkalis, but dissolves in concentrated sulphuric acid to a blue solution, and may be obtained from its solution in nitrobenzene as a brown, crystalline powder.



I.



II.

4:4′-Dichloro-2:2′-dimethyl-1:1′-dianthraquinonyl and 2:4:2′:4′-tetramethyl-1:1′-dianthraquinonyl furnish similar condensation products. G. T. M.

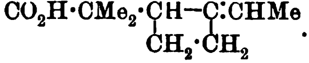
The Constituents of Ethereal Oils. Frederich W. Semmler and Konrad Bartelt (*Ber.*, 1907, 40, 432—440. Compare this vol., i, 11).—I. γ- and *α-Fencholenic acids.*—The α-fencholenic acid obtained from fenchone oxime by the action of dehydrating agents and hydrolysis (Cockburn, Trans., 1899, 75, 501) and that from bromofenchone by the action of alcoholic potassium hydroxide (Czerny, Abstr., 1900, i, 675), are not identical, although their amides and hydrochlorides melt at the same temperature. The acid derived from bromofenchone is called *γ-fencholenic acid*, $C_{10}H_{16}O_2$, and has b. p. 145—146°/10 mm., D^{20} 1·0087, n_D 1·47838, α_D + 52°·30′ (100 mm.). The *ammonium* salt, m. p. 125°, when heated at 180° under pressure, yields the amide, m. p. 113—114°, which does not depress the melting point of the amide from α-fencholenic acid. Reduction of the acid with hydrogen iodide and red phosphorus at 180° under pressure gives a mixture of hydrocarbons, C_9H_{18} or $C_{10}H_{20}$, b. p. 48°/20 mm., D^{20} 0·7794, n_D 1·43155, and an acid, b. p. 280° in a vacuum. When heated under pressure at 160° with alcoholic potassium hydroxide, the rotation of γ-fencholenic acid falls to α_D + 43°, or on treatment with acids to + 41·65°; it also falls when kept for three months, but it never becomes as low as that of α-fencholenic acid, $[\alpha]_D$ 32°·35′.

γ-Fencholenic acid in benzene solution and water, when treated with ozone and then distilled in a vacuum, gives a monobasic ketonic *acid*, $C_8H_{12}O_3$, in quantitative yield, b. p. 185—187°/10 mm., D^{22} 1·121, n_D 1·47936 α_D + 22°·30′ tube (100 mm.) in 25% alcohol solution. The *semicarbazone*, $C_9H_{15}O_3N_3$, m. p. 190°, crystallises from methyl alcohol. When oxidised with alkaline potassium permanganate an *acid*, b. p. 210—215°/8 mm. (decomp.), is obtained. On the other hand, no ketonic acid could be isolated when α-fencholenic acid is oxidised by ozone, the product obtained has b. p. 140—230°/10 mm., the chief fraction, b. p. 210—215°. This behaviour shows that α- and γ-fencholenic acids are not identical, but if γ-fencholenic acid is treated with acid or alkalis and then oxidised with ozone, not a trace of ketonic acid can be isolated, the product has b. p. 140—230°/10 mm.

When shaken with dilute sodium hydroxide for one hundred days, the lactone from γ-fencholenic acid of b. p. 122—123°/9 mm. and m. p. 77—78° (Czerny, *loc. cit.*) gives *hydroxydihydrofencholenic acid*, $C_{10}H_{18}O_3$, m. p. 105—107°, which is monobasic and yields a soluble *silver* and a sparingly soluble *copper* salt. The lactone is regenerated along with an unsaturated acid, b. p. 143°/10 mm., probably α-fencholenic acid, by treatment with dilute sulphuric acid. This lactone is identical with that obtained from the α-acid, as it shows no depression in m. p. when mixed with it, and also on reduction with sodium and alcohol yields the same *glycol*, $C_{10}H_{22}O_2$, b. p. 158—161°/11 mm., m. p. 58—60°.

The following constants of bromofenchone have been redetermined (compare Czerny, *loc. cit.*, and Balbiano, Abstr., 1901, i, 89), b. p. 125—130°/10 mm., D^{22} 1·3005, n_D 1·50605, α_D + 10—12° (100 mm.).

Constitution of Fenchone.—Polemical. A reply to Kondakoff (Abstr., 1906, i, 520). A table is also given showing how, by the use of Semmler's formula for fenchone, these compounds are derivable, that of γ-fencholenic acid is



$$\begin{array}{l} CO_2H\cdot CMe_2\cdot \underset{|}{C}H-\underset{|}{C}{:}CHMe \\ \qquad\qquad\qquad\quad CH_2\cdot CH_2 \end{array}.$$

W. R.

Terpineol of Majorana Oil. Otto Wallach and Friedrich Bödecker (*Ber.*, 1907, 40, 596—600).—On oxidising the terpineol fraction of majorana oil (compare this vol., i, 65) with permanganate a *ketone* is formed of which the *semicarbazone* melts at 145—146°. The glycerol, $C_{10}H_{17}(OH)_3$, is more sparingly soluble in chloroform and crystallises otherwise than the isomeric trioxyterpane; on further oxidation it gives rise to *acids*, $C_{10}H_{18}O_6$, m. p. 205—206° and 188—189°, which form *lactones*, m. p. 63—64° and 72—73° respectively. On shaking the terpineol fraction of majorana oil with sulphuric acid, *cis*-terpinene hydrate, m. p. 117°, and terpinene-terpine, m. p. 137°, are obtained along with mixed crystals of these two substances, m. p. 108° (about). The paper concludes with the discussion of a formula for terpineol. E. F. A.

Combination of Glycuronic Acid with Optical Antipodes. ADOLF MAGNUS-LEVY (*Biochem. Zeitsch.*, 1907, **2**, 319—331).—Experiments made on dogs and rabbits indicate that both *d*- and *l*-borneol and *d*- and *l*-camphor readily combine with glycuronic acid, and the animal organism appears to be incapable of differentiating between the stereoisomerides. Inactive methylethylpropylcarbinol as it combines with *d*-glycuronic acid during its passage through the organism is not resolved into active components.

l-*Camphorglycuronic acid*, $C_{16}H_{24}O_8$, is most readily isolated from the urine of dogs fed with *l*-camphor by conversion into its *strychnine* salt, $C_{37}H_{40}O_{10}N_2,2H_2O$, m. p. 189—195° (decomp.). The free acid contains water of crystallisation, and melts between 120° and 130°. When hydrolysed with 10% sulphuric acid, the complex glycuronic acid yields l-*camphorol*, $C_{10}H_{16}O_2$, m. p. 207—210° (not sharp), $[\alpha]_D$ $-32{\cdot}93°$; its *semicarbazone* melts and decomposes at 235—240°.

Sodium l-*borneolglycuronate*, $C_{16}H_{25}O_7Na,H_2O$, has $[\alpha]_D^{20}$ $-66{\cdot}5°$.

Hydroxycamphorglycuronic acid, $C_{16}H_{24}O_8,H_2O$, obtained from the urine of a dog fed on Manasse's hydroxycamphor (oxaphor), m. p. 212—213°, crystallises from water in glistening plates, m. p. 138°, and the sodium salt has $[\alpha]_D$ $-32{\cdot}7°$. When hydrolysed it yields hydroxycamphor. J. J. S.

Boiling Point and the Nature of Dipentene. OTTO WALLACH (*Ber.*, 1907, **40**, 600—606).—The author had shown previously that whereas dipentene prepared as pure as possible has b. p. 177—178°, *i*-limonene, prepared by mixing *d*- and *l*-limonenes, has b. p. 175—176° (compare Abstr., 1888). Semmler's criticisms (*Ber.*, 1906, **39**, 4427) have led him again to purify very carefully dipentene dihydrochloride, heat this with aniline and remove the aniline by steam distillation, the liquor being rendered acid by oxalic acid. The carefully purified dipentene had b. p. 177—178° for the greater part of the distillate, and 10 grams yielded but 8·5 grams of solid tetrabromide, whereas *i*-limonene yielded 10 grams under like conditions. It is considered that dipentene contains another hydrocarbon which cannot be separated from it by distillation, and which, perhaps, represents ψ-limonene.

E. F. A.

Terpinenes. OTTO WALLACH (*Ber.*, 1907, **40**, 575—584).—By the interaction of terpinene dihydrochloride and potassium hydroxide (compare this vol., i, 64), a *terpineol*, $C_{10}H_{17}{\cdot}OH$, and a *terpin*,

$$C_{10}H_{16}(OH)_2,$$

m. p. 136·5—137·5°, are obtained along with von Baeyer's γ-terpineol (m. p. 69°), and *cis*-terpine (m. p. 117°) and *trans*-terpine (m. p. 156°).

γ-Terpineol yields a mixture of *cis*- and *trans*-terpines on shaking with acids as also, though more slowly, when acted on by potassium hydroxide. The terpins obtained above, therefore, probably originate from γ-terpineol. The terpin (m. p. 137°) is easily obtained by shaking the corresponding terpineol with sulphuric acid (compare following abstract). It has b. p. 250°, and crystallises in optically inactive characteristic plates.

Terpinene nitrosite when reduced in glacial acetic acid solution, at first at 0° and subsequently at the temperature of the water-bath, yields a considerable quantity of carvenone. A still better yield of carvenone is obtained on reducing under the same conditions terpinenenitrolepiperidide (m. p. 231—232°); whereas the semicarbazone, oxaminooxime, and benzoate of the oxime of the compound obtained all agree with the corresponding carvenone derivatives, the oxime has always a lower m. p.

The paper concludes with a discussion of this reaction and a further consideration of the constitution of terpinene. E. F. A.

Sabinene and its Relationship to Terpinene. OTTO WALLACH (*Ber.*, 1907, **40**, 585—595).—The paper is largely of a polemical nature, being a reply to Semmler (this vol., i, 145). Attention is again directed to the high value of the molecular refraction of sabinene, due possibly to the presence of a methylene group in a semicyclic ring. The same solid dichloride is formed whether sabinene is treated with hydrogen chloride in acetic acid or in moist ethereal solution; in dry ether no formation of hydrochloride takes place, just as in the case of limonene. In carbon disulphide solution sabinene forms a *monohydrochloride*, b. p. 87—92°/12 mm., D 0·982, n_D^{20} 1·4824, which does not yield a sparingly soluble nitrosate, but forms a *nitrosochloride* decomposed by bases into *nitrolamines*. This monohydrochloride is converted by hydrogen chloride in acetic acid solution into the dichloride.

Sabinene when shaken with sulphuric acid yields a terpin, $C_{10}H_{18}(OH)_2$, m. p. 137°, and a terpineol, $C_{10}H_{17}\cdot OH$, b. p. 209—212°, D 0·9265, n_D^{19} 1·4785, which forms a dichloride, $C_{10}H_{16},2HCl$, m. p. 52°, and is converted by permanganate into the glycerol already described (this vol., i, 64) from cardamom and majorana oils. The author claims priority over Semmler (*loc. cit.*) on these points. E. F. A.

Russian Peppermint Oil. IWAN SCHINDELMEISER (*Chem. Centr.*, 1906, ii, 1764; from *Apoth.-Zeit.*, 21, 927—928).—A sample of peppermint oil from Tambow, which had D^{19} 0·908, $[\alpha]_D$ $-21°48'$, and n_D 1·46108, was soluble in 4 parts of 70% and in 0·5 of 95% alcohol. The oil solidified when cooled with sodium chloride and ice for a long time. The aqueous solution of an aldehyde, which distilled at 115—120° when treated with silver oxide, yielded an acid the silver salt of which contained 61% of silver. The oil contained *i*-pinene and more *l*-limonene than *d*-limonene, but neither phellandrene nor menthene was present (compare Andréeff and Andres, Abstr., 1892, i, 723). Cineol was separated by means of syrupy phosphoric acid, and 16·36% of *l*-menthone, $[\alpha]_D$ − 23°4·5′, was isolated. The oil yielded 51·22% of a mixture of free *l*- and *d*-menthols, in which the former was present in the greater quantity, and 4·8% of the menthyl esters of acetic and baldrianic acids calculated as acetate. A small quantity of a sesquiterpene was also obtained, but paucity of material prevented identification. E. W. W.

α- and β-Amyrins from Bresk. N. H. Cohen (*Proc. K. Akad. Wetensch. Amsterdam*, 1906, 9, 471. Compare Romburgh and Cohen, Abstr., 1906, 197; Vesterberg, Abstr., 1891, 165).—α-Amyrin, m. p. 186° (corr.), has now been obtained from bresk or djelutung; it has $[\alpha]_D$ + 82·6° in chloroform, or + 88·2° in benzene solution. The acetate, m. p. 224—225° (corr.), has $[\alpha]_D$ + 75·8° in chloroform solution; the benzoate, m. p. 195° (corr.); the *cinnamate* crystallises in small, hard needles, m. p. 178° (corr.).

β-Amyrin cinnamate crystallises from acetone in small needles, m. p. 241° (corr.). G. Y.

Solubility of Salicin. David B. Dott (*Pharm. J.*, 1907, [iv], 24, 79).—Salicin is soluble to the extent of 1 part in 24 parts of water at 25°. E. G.

Elaterin. Franz von Hemmelmayr (*Monatsh.*, 1906, 27, 1167—1182. Compare Abstr., 1906, i, 973; Thoms, *Chem. Zeitsch.*, 1906, 923; Pollak, Abstr., 1906, i, 973).—The analytical results obtained by the author and by Berg (Abstr., 1906, i, 596) with elaterin, diacetylelaterin, bromoelaterin, elaterin diphenylhydrazone, and elateridin are tabulated and found to agree best with the formula, $C_{24}H_{34}O_6$, for elaterin, to which in agreement with its properties is now ascribed the extended formula, $C_{20}H_{29}(CO)_2(OH)_2{\cdot}OAc$. The formula for elateridin derived from this should contain two hydroxyl groups; as, however, elateridin forms only a monoacetyl derivative which is not identical with elaterin, its molecule must undergo some isomeric change during its formation.

The bromo-derivative of elaterin, $C_{24}H_{33}O_6Br$, prepared by the action of bromine on elaterin in glacial acetic acid solution, forms a yellow, amorphous powder, m. p. 112°, but decomposes at 118°. The diacetyl derivative, $C_{24}H_{32}O_6Ac_2$, m. p. 124°. The diphenylhydrazone, $C_{36}H_{46}O_4N_4$, forms a yellow, amorphous mass, commences to sinter at 158°, and decomposes and evolves gas at 170°.

Elateridin, $C_{22}H_{32}O_5$, which sinters at 130°, m. p. 140—150°, gives a reddish-brown coloration with alcoholic ferric chloride, and is soluble in aqueous potassium hydroxide only with difficulty. The *monoacetyl* derivative, $C_{22}H_{31}O_5Ac$, formed by boiling elateridin with acetic anhydride and sodium acetate, is obtained as a yellow, amorphous mass, sinters at 130°, m. p. 140—150°.

Elateric acid, $C_{22}H_{32}O_6,1\frac{1}{2}H_2O$, m. p. 70—80°; the *methyl* ester, $C_{22}H_{31}O_6Me$, m. p. 85—90°. When boiled with phenylhydrazine and acetic acid in alcoholic solution, elateric acid forms a resinous *compound*, $C_{28}H_{38}O_5N_2$ or $C_{28}H_{40}O_6N_2$, which sinters at 125°, m. p. about 140°.

Oxidation of elaterin with chromium trioxide in glacial acetic acid solution leads to the formation of a *product* which sinters at 100°, m. p. 115—120°, and dissolves without change in aqueous potassium hydroxide or carbonate. G. Y.

Dyeing and Ionisation. LÉO VIGNON (*Compt. rend.*, 1907, **144**, 81—83).—The author has shown previously (this vol., i, 102) that the chemical activity of textile fibres of animal origin towards acids, bases, or salts increases with the dilution, and consequently with the electrolytic dissociation of the solutions employed; in the present paper it is shown that the electrolytic dissociation of dyes, except in the case of picric acid, increases with the dilution of the solution and also with the temperature; the experiments were conducted on solutions of roccellin, orange II, magenta, and picric acid, and the results are tabulated in the original. M. A. W.

Process of Dyeing Animal Textile Fibres. III. P. GELMO and WILHELM SUIDA (*Monatsh.*, 1906, **27**, 1193—1198. Compare Abstr., 1905, i, 714; 1906, i, 445).—The experiments described in this paper were performed with the same wool as was employed in the previous series. Samples of the wool were boiled with alcoholic sulphuric, hydrochloric, and phosphoric acids and thoroughly washed; half of each was titrated with *N*/10 sulphuric acid, *N*/10 hydrochloric acid, and *N*/10 ammonia respectively; the remaining half samples were boiled with aqueous ammonium carbonate and then titrated. Ammonia, hydrochloric acid, and sulphuric acid were absorbed in the proportions: after treatment with alcoholic sulphuric acid,

$$NH_3 : 1{\cdot}34HCl : 1{\cdot}83H_2SO_4/2;$$

after treatment with alcoholic hydrochloric acid,

$$NH_3 : 4{\cdot}4HCl : 4{\cdot}62H_2SO_4/2;$$

or after treatment with alcoholic phosphoric acid,

$$NH_3 : 3{\cdot}95HCl : 4{\cdot}34H_2SO_4/2.$$

After the further treatment with ammonium carbonate, these three samples absorbed ammonia, hydrochloric acid, and sulphuric acid in the proportions: $NH_3 : 12{\cdot}5HCl : 13{\cdot}4H_2SO_4/2$; $NH_3 : 8HCl : 8{\cdot}9H_2SO_4/2$; and $NH_3 : 5{\cdot}46HCl : 6{\cdot}01H_2SO_4/2$ respectively. The results of a number of dyeing experiments showed that after treatment with alcoholic acids, wool gives intense shades with acid, but only weak shades with basic, dyes. This effect was least pronounced in the wool treated with phosphoric acid.

A sample of wool treated with hydrogen chloride in absolute alcohol and thoroughly washed with alcohol and water was not dyed by basic dyes, but with acid dyes gave intense shades fast to soaping. Wool treated successively with alcoholic hydrogen chloride and ammonium carbonate was dyed feebly by basic, but intensely by acid, dyes, the shades being removed almost entirely by soaping.

N/10 ammonia, *N*/10 hydrochloric acid, and *N*/10 sulphuric acid were absorbed by wool which had been treated with 1% of its weight of sodium nitrite in the proportion $NH_3 : 5{\cdot}9HCl : 7{\cdot}1H_2SO_4/2$, or by wool treated with a 1% solution of sodium nitrite in the proportion $NH_3 : 2{\cdot}12HCl : 2{\cdot}69H_2SO_4/2$. Wool treated with even traces of nitrous acid has no affinity for coal-tar dyes, but on exposure to light becomes yellow to intense brownish-orange, depending on the amount of nitrous acid, the shades being rendered more intense by addition of alkali hydroxides.

No difference could be detected in the behaviour in a neutral dye-bath of untreated wool and wool treated with phosphorus trichloride.

G. Y.

Sulphur Dyes. HERMANN WICHELHAUS [and, in part, VIEWEG] (*Ber.*, 1907, **40**, 126—129).—Many natural, non-nitrogenous colouring matters such an brazilin, hæmatoxylin, maclurin, euxanthone, &c., are transformed into sulphur dyes when heated with sulphur in the absence of air, hydrogen sulphide and to a certain extent sulphur dioxide being evolved. The dyes dissolve in sodium sulphide solution, yielding brown to black tones.

Artificial phenolic dyes of the type of gallacetophenone, aurin, and fluorescein may be transformed into sulphur dyes by a similar process. A stable dye containing 27% of sulphur is formed when fluorescein or a mixture of phthalic anhydride and resorcinol is fused with sulphur at 250—280° for six to eight hours. Similar products may be obtained from di- and tetra-chlorophthalic acids.

J. J. S.

Oximes of Methylfurfuraldehyde. K. FROMHERZ and WILHELM MEEGEN (*Ber.*, 1907, **40**, 403—406).—When methylfurfuraldehyde is treated with hydroxylamine according to Goldschmidt and Zanoli's method (Abstr., 1892, i, 1433), a product is obtained which is regarded as a mixture of the *syn-* and *anti*-aldoximes. When crystallised from light petroleum it melts at 51—52°, but when repeatedly recrystallised it yields a small amount of pure syn-*methylfurfuraldoxime*, $C_6H_7O_2N$, in the form of colourless, glistening needles, m. p. 110°. The same compound may also be obtained by converting the mixture of oximes into the hydrochloride and decomposing this with alkali. The *phenylcarbimide* derivative, $C_{10}H_{12}O_3N_2$, exists in two modifications, a yellow, labile form, m. p. 101° (decomp.), and a colourless, stable form, m. p. 106—109°.

The pure *anti*-oxime has not been obtained.

J. J. S.

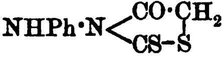
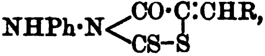
Mixed Anhydrides of Tannic and Cinnamic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 173729).—A product containing mono- and di-acetyltannic-cinnamic anhydrides is obtained by heating together at 100° acetic anhydride, tannic acid, and cinnamic acid, and gradually adding phosphorus pentachloride to the mixture. The heating is continued until the product yields neither cinnamic nor tannic acid on treatment with warm water; the mixture is then washed successively with cold and hot water until the filtrate has a neutral reaction. The residue, which is dried at 45°, is soluble in alcohol, and reprecipitated in an amorphous form by water. Although stable in hot water, the mixed anhydrides are hydrolysed by dilute alkalis.

G. T. M.

Pyrone Hydroperbromides. Arthur Hantzsch and O. Denstorff (*Ber.*, 1907, **40**, 241—243. Compare Abstr., 1906, i, 745).—Reply to Feist (Abstr., 1906, i, 974). C. S.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. V. Rudolf Andreasch (*Monatsh.*, 1906, **27**, 1211—1222. Compare Abstr., 1903, i, 855; 1904, i, 444; 1905, i, 930, 933).—The action of ethyl chloroacetate on ammonium phenyldithiocarbazinate (Heller and Bauer, Abstr., 1902, i, 444) leads to the formation of *ethyl phenyldithiocarbazinacetate*,

$$NHPh\cdot NH\cdot CS\cdot S\cdot CH_2\cdot CO_2Et,$$

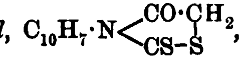
which crystallises in long needles, m. p. 108—109°, and *3-anilinorhodanic acid*,  $NHPh\cdot N<\begin{matrix}CO\cdot CH_2\\ CS-S\end{matrix}$. This forms yellow, granular crystals, m. p. 125°, and is less soluble in alcohol than the carbazinate from which it is formed by heating at 100°, or by boiling with glacial acetic acid and acetic anhydride. The following condensation products of phenylrhodanic acid and aldehydes,  $NHPh\cdot N<\begin{matrix}CO\cdot C{:}CHR\\ CS-S\end{matrix}$, are formed by heating the rhodanic acid or the ethyl carbazinate with the aldehyde and glacial acetic acid.

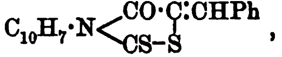
R = Ph: slender, yellow needles, m. p. 195°; R = $\cdot C_6H_4\cdot OH$ (*o*): yellow, pointed needles, m. p. 170—173°; R = $\cdot C_6H_4\cdot NMe_2$ (*p*): microscopic, scarlet needles, m. p. 219°; R = $\cdot C_4OH_3$: yellow needles, m. p. 168°.

Bargellini's work on the condensation of aldehydes with rhodanic acids (Abstr., 1906, i, 383, 536) is criticised.

The action of ethyl chloroformate on ammonium phenyldithiocarbamate in alcoholic solution leads to the formation of phenylthiocarbamide, carbamide, carbanilide, and a *substance*, m. p. below 100°. Ethyl chlorocarbonate and ammonium phenyldithiocarbamate interact, forming phenyl thiocarbimide, carbon oxysulphide, and ammonium chloride. G. Y.

Substituted Rhodanic Acids and their Aldehyde Condensation Products. VI. Alois Wagner (*Monatsh.*, 1906, **27**, 1233—1244. Compare Abstr., 1903, i, 855; 1904, 444; 1905, i, 930, 933, and preceding abstract).—Andreasch and Zipser having suggested the use of rhodanic acids in the estimation of furfuraldehyde, the author has investigated the suitability of some higher substituted rhodanic acids, but found this to be less than that of phenylrhodanic acid. When pure, the rhodanic acids now described do not condense with aldehydes even in presence of glacial acetic or concentrated sulphuric acid; the condensation products are obtained, however, from the crude ethyl substituted dithiocarbaminacetates formed as intermediate products in the action of ethyl chloroacetate on the substituted dithiocarbamates.

3-a-Naphthylrhodanic acid,  $C_{10}H_7\cdot N<\begin{matrix}CO\cdot CH_2\\ CS-S\end{matrix}$, prepared together with *s*-di-*a*-naphthylcarbamide by the action at 100° of ethyl chloroacetate on ammonium α-naphthyldithiocarbamate obtained from α-naphthylamine, carbon disulphide, and concentrated aqueous ammonia, crystallises in colourless, tetragonal leaflets, m. p. 167—168°. *Ethyl α-naphthyldithiocarbaminacetate*, $NHPh\cdot CS\cdot S\cdot CH_2\cdot CO_2Et$, is formed if the action of ethyl chloroacetate on ammonium α-naphthyldithiocarbamate takes place below 100°; it crystallises in large, white needles, m. p. 81°. 3-α-*Naphthyl*-5-*benzylidenerhodanic acid*,

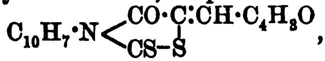


$$C_{10}H_7\cdot N{<}\begin{matrix}CO\cdot C{:}CHPh\\ CS-S\end{matrix},$$

crystallises in long, yellow needles, m. p. 159°. The *furfurylidene* derivative is obtained as an oil.

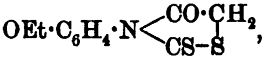
The corresponding β-naphthyl and *p*-ethoxyphenyl compounds were prepared in the same manner.

3-β-*Naphthylrhodanic acid*, $C_{13}H_9ONS_2$, formed together with *s*-di-β-naphthylthiocarbamide, crystallises in microscopic, brown, pointed needles, m. p. 180—190°. *Ethyl β-naphthyldithiocarbaminacetate*, $C_{15}H_{15}O_2NS_2$, crystallises in needles, m. p. 83°. 3-β-*Naphthyl*-5-*benzylidenerhodanic acid*, $C_{20}H_{13}ONS_2$, crystallises in microscopic, yellow leaflets, m. p. 202°. 3-β-*Naphthyl*-5-*furfurylidenerhodanic acid*,



$C_{10}H_7\cdot N{<}\begin{matrix}CO\cdot C{:}CH\cdot C_4H_3O\\ CS-S\end{matrix}$, crystallises in slender, yellow needles, m. p. 208°.

3-p-*Ethoxyphenylrhodanic acid*,



$OEt\cdot C_6H_4\cdot N{<}\begin{matrix}CO\cdot CH_2\\ CS-S\end{matrix}$, crystallises in long, yellowish-white needles, m. p. 180—188°. The 5-*benzylidene* derivative, $C_{18}H_{15}O_2NS_2$, forms long, sulphur-yellow needles, m. p. 212—214°. The 5-*furfurylidene* derivative, $C_{14}H_{13}O_3NS_2$, crystallises in long, chrome-yellow needles, m. p. 197°. G. Y.

Derivatives of Hordenine. Eugène Léger (*Compt. rend.*, 1907, **144**, 208—210. Compare Abstr., 1906, i, 204, 761; this vol., i, 151).—The following derivatives of hordenine acting (1) as a tertiary amine, (2) as a phenol, and (3) as both amine and phenol are described. The *normal tartrate*, $(C_{10}H_{15}ON)_2,C_4H_6O_6$, anhydrous needles; the *hydrogen tartrate*, $C_{10}H_{15}ON,C_4H_6O_6$, anhydrous needles; *hordenine methochloride*, $(C_{10}H_{15}ON),MeCl$, anhydrous needles; *hordenine ethochloride*,

$$C_{10}H_{15}ON,EtCl,$$

anhydrous needles; *hordenine ethobromide*, $C_{10}H_{15}ON,EtBr$, square plates; *hordenine ethiodide*, $C_{10}H_{15}ON,EtI$, anhydrous, prismatic needles; *benzoylhordenine hydrochloride*, $C_{10}H_{14}BzON,HCl$, anhydrous needles; *benzoylhordenine hydrobromide*, $C_{10}H_{14}BzON,HBr$, brilliant, rectangular lamellæ; *cinnamoylhordenine*, long slender, needles, m. p. 55·8° (corr.) (partial decomp.), but forming stable salts which crystallise easily; *cinnamoylhordenine hydrochloride*,

$$C_{10}H_{14}(C_9H_7O)ON,HCl,H_2O,$$

prismatic needles; *anisylhordenine hydrochloride*,

$$C_{10}H_{14}(C_8H_7O_2)ON,HCl,H_2O,$$

large, efflorescent plates. *Methylhordenine methiodide*,

$$OMe\cdot C_6H_4\cdot[CH_2]_2\cdot NMe_3I,$$

slender, white, felted needles containing $1\frac{1}{2}H_2O$. E. H.

Preparation of Acetyl Derivatives of Morphine Bases. KNOLL & Co. (D.R.-P. 175068).—By treating morphine bases with sulphoacetic acid or a mixture of acetic anhydride and sulphuric acid, a series of new acetyl derivatives has been obtained. *Triacetylmorphine*, m. p. 206—208°; *diacetylcodeine*, m. p. 145—146°, and *dibenzoylacetylmorphine* (from dibenzoylmorphine), m. p. 166—168°, are described. G. T. M.

Behaviour of Chlorocodide on Reduction. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, **40**, 376—377. Compare Göhlich, Abstr., 1894, i, 431; Vongerichten and Müller, Abstr., 1903, i, 571).—On reduction with sodium and ethyl or amyl alcohol, or with tin or zinc dust and hydrochloric acid, chlorocodide yields *deoxycodeine*,

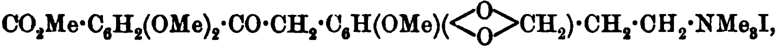
$$C_{18}H_{21}O_2N,\tfrac{1}{2}H_2O,$$

which crystallises in shining leaflets, loses $\tfrac{1}{2}H_2O$ above 100°, m. p. about 126° (decomp.) when quickly heated; the anhydrous substance is vitreous. It forms crystalline salts; the *hydrochloride* separates from alcohol in prisms, m. p. about 165° (decomp.). G. Y.

Melting Point of Cotarnine. DAVID B. DOTT (*Pharm. J.*, 1907, [iv], **24**, 78—79).—Freshly prepared cotarnine, purified by crystallisation from benzene, has m. p. 125° (decomp.). When the crystalline base is heated on the water-bath, it loses weight equivalent to more than 1 mol. H_2O and then melts at 100°. It is therefore considered that the m. p. of cotarnine is of little value as a test for purity.
E. G.

Preparation of Cotarnine Phthalates. KNOLL & Co. (D. R.-P. 175079).—*Cotarnine phthalate*, m. p. 102—105°, is obtained by mixing 237 parts of cotarnine and 83 parts of phthalic acid in aqueous or methyl alcoholic solution, and concentrating under reduced pressure. *Cotarnine hydrogen phthalate*, produced by mixing alcoholic solution of sodium hydrogen phthalate and cotarnine hydrochloride, is obtained from the solution, after removing sodium chloride, in well-defined, yellow crystals, m. p. 115°. The normal salt when recrystallised from alcohol tends to decompose into the acid salt and free base.
G. T. M.

Narceine. MARTIN FREUND [and BESCHKE] (*Ber.*, 1907, **40**, 194—204. Compare Freund and Frankforter, Abstr., 1894, i, 58).—The author has repeated the alkylation of narceine by the action of methyl and ethyl iodides on sodium narceine, and confirms Tambach and Jäger's statement that the alcohol used as solvent is without influence on the nature of the product (Abstr., 1906, i, 879); contrary, however, to these authors' view it is found that the product of methylation, m. p. 208—209°, is the narceinium methiodide methyl ester,



$$CO_2Me\cdot C_6H_2(OMe)_2\cdot CO\cdot CH_2\cdot C_6H(OMe)(<\substack{O\\O}>CH_2)\cdot CH_2\cdot CH_2\cdot NMe_3I,$$

and not methylnarceinium methiodide, whilst similarly the product of ethylation, ($+H_2O$), m. p. 141° or, ($+C_2H_6O$), m. p. 181, is narceinium ethiodide ethyl ester, $CO_2Et\cdot C_{20}H_{20}O_6\cdot NMe_2EtI$, and not ethylnarceinium ethiodide. The formulæ given by Tambach and Jäger for the remainder of their products of narceine must be altered in the same sense.

Narceinium methiodide, formed by heating narceine with methyl iodide at 100°, and described previously as a resin (Freund and Frankforter, *loc. cit.*), crystallises from water in needles, m. p. 207°, and when boiled with aqueous alkalis yields trimethylamine and narceonic acid, m. p. 217° (208°, *loc. cit.*).

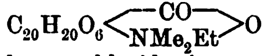
The product formed by heating narceine with methyl sulphate and alcohol (Tambach and Jäger) is narceinium hydrogen methosulphate, $C_{23}H_{27}O_8N,MeHSO_4$, which is decomposed by water, forming narceine.

The action of 1 mol. of methyl sulphate on sodium narceine leads to the formation of the sodium salt of methylnarceinium methosulphate, $CO_2Na\cdot C_{20}H_{20}O_6\cdot NMe_3\cdot SO_4Me$, which on treatment with hydrochloric acid yields narceinium methochloride,

$$CO_2H\cdot C_{20}H_{20}O_6\cdot NMe_3Cl,$$

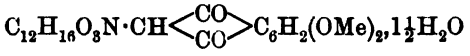
m. p. 243°; this is converted by potassium iodide into the methiodide, m. p. 207°.

The product, m. p. 184—186°, of the action of 2 mols. of methyl sulphate on sodium narceine is the *additive* compound of methyl sulphate and narceine methyl ester; it is converted by potassium iodide into the methyl ester of narceinium methiodide which is insoluble in aqueous alkalis.

Ethyl sulphate (1 mol.) and sodium narceine yield sodium narceinium ethosulphate, which on treatment with hydrochloric acid forms narceinium ethochloride, $CO_2H\cdot C_{20}H_{20}O_6\cdot NMe_2EtCl$, m. p. 231°; this is converted by boiling aqueous alkalis into narceonic acid. The base, m. p. 175—177°, obtained from the ethochloride, is probably the betaine,  $C_{20}H_{20}O_6<{\substack{CO\\NMe_2Et}}>O$. The ethochloride is converted by alcoholic hydrogen chloride into narceinium ethochloride ethyl ester, $CO_2Et\cdot C_{20}H_{20}O_6\cdot NMe_2EtCl$, m. p. 218—219°, which is formed also by the action of silver chloride on the ethyl ester of narceinium ethiodide; this yields narceonic acid when boiled with aqueous alkalis.

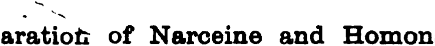
The product (m. p. 191—193°: Tambach and Jäger, *loc. cit.*) of the action of ethyl iodide on narceine ethyl ester is narceinium ethiodide ethyl ester, m. p. 181° when recrystallised from alcohol.

The action of sodium methoxide on narceine ethyl ester in methyl alcoholic solution leads to the formation of narcindonine,



$$C_{12}H_{16}O_3N\cdot CH<{\substack{CO\\CO}}>C_6H_2(OMe)_2,1\tfrac{1}{2}H_2O$$

which is formed also, together with narceine, by the action of sodium methoxide on *apo*narceine (compare Freund and Michaels, Abstr., 1895, i, 630; Eibner, Abstr., 1906, i, 588); it crystallises in red plates, m. p. 168—169°, loses $1\frac{1}{2}H_2O$ at 110°, and then has m. p. 174°.

Tambach and Jäger's *apo*narceine is considered to be probably the lactone,  $C_{12}H_{16}O_3N\cdot CH:C<{\substack{O\\C_6H_2(OMe)_2}}>CO$.

G. Y.

Preparation of Narceine and Homonarceine Derivatives.

KNOLL & Co. (D.R.-P. 174380).—The alkali derivatives of narceine and homonarceine, or the corresponding compounds with the alkali earth metals, when treated with methyl or ethyl sulphate give rise to new alkyl derivatives of these bases in which the carboxyl group is still unesterified.

Narceine dissolved in *N*-sodium hydroxide and treated with methyl sulphate furnishes a base the salt of which crystallises from alcohol, m. p. 242°. This compound when esterified with alcoholic hydrogen-chloride, yields an *ester hydrochloride*, m. p. 214—216°; *platinichloride*, m. p. 220°.

Narceine and ethyl sulphate give rise to a similar base: *hydrochloride*, m. p. 231°; *hydrochloride* of *ethyl ester*, m. p. 219°.

The base from homonarceine and methyl sulphate has the following derivatives: *hydrochloride*, m. p. 231—232°; *platinichloride*, m. p. 181—182°; *hydrochloride* of *ethyl ester*, m. p. 212—214°. Homonarceine and ethyl sulphate give a similar ethyl derivative: *hydrochloride*, m. p. 211°. G. T. M.

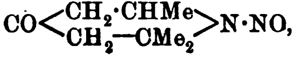
Tertiary and Quaternary Bases from Piperidine. II. SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1907, **40**, 424—427. Compare Abstr., 1906, i, 881; Gabriel and Stelzner, 1896, i, 702; Hörlein and Kneisel, 1906, i, 458).—1-γ-*Hydroxypropylpiperidine*, $C_5H_{10}N\cdot[CH_2]_2\cdot CH_2\cdot OH$, obtained by heating 2 parts of trimethylenechlorohydrin with 4 parts of piperidine for one hour at the temperature of the water-bath and then liberating the base with potassium hydroxide, is a colourless oil, b. p. 225—228°/759 mm. The base is precipitated from its aqueous solution by potassium hydroxide. The *hydrochloride* is precipitated from alcoholic solution by acetone as a crystalline, hygroscopic powder, m. p. 151°; the *aurichloride* forms golden-yellow, hexagonal plates, m. p. 69—70°. When heated with hydrochloric acid at 150°, the base is converted into 1-γ-chloropropylpiperidine.

By repeated fractionation of the portion distilling at 200—300°, obtained in the interaction of the quaternary salt and potassium hydroxide (*loc. cit.*), an oil, b. p. 224—227°, was isolated and identified as 1-γ-hydroxypropylpiperidine. The chief product of this interaction, dipiperidinopropyl ether, is formed either by the condensation of the 1-γ-chloropropylpiperidine and γ-hydroxy base, or by dehydration of the base.

1-δ-*Chlorobutylpiperidine hydrochloride*, $C_5H_{10}N\cdot[CH_2]_4Cl,HCl$, crystallises from acetone in colourless needles, m. p. 167°. W. R.

Nitroso-derivatives of Cyclic Acetone Bases. MORITZ KOHN and FRANZ WENZEL (*Monatsh.*, 1906, **27**, 981—986. Compare Heintz, this Journal, 1877, ii, 428; Fischer, Abstr., 1884, 1290; Antrick, Abstr., 1885, 502).—Nitroso-derivatives have been obtained from vinyldiacetonamine, *iso*butylidenediacetonamine, and benzylidenediacetonamine by the action of potassium nitrite on the hydrochloride of the base in aqueous solution.

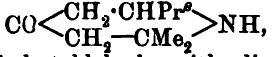
1-*Nitroso*-2 : 2 : 6-*trimethylpiperidone* (*nitrosovinyldiacetonamine*),



$$CO<\begin{matrix}CH_2\cdot CHMe\\ CH_2-CMe_2\end{matrix}>N\cdot NO,$$

crystallises from dilute methyl alcohol in light yellow, rhombic plates, [$a:b:c = 0{\cdot}9878:1{\cdot}0932:1$ or $a:b:c = 0{\cdot}6585:0{\cdot}7288:1$], m. p. 58—59°.

2 : 2-*Dimethyl*-6 iso*propylpiperidone* (iso*butylidenediacetonamine*),

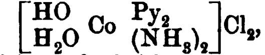


$$\mathrm{CO}<\begin{matrix}\mathrm{CH_2\cdot CHPr^{\beta}}\\ \mathrm{CH_2{-}CMe_2}\end{matrix}>\mathrm{NH},$$

prepared by boiling *iso*butaldehyde with diacetonamine oxalate in alcoholic solution, is obtained as a slightly yellow oil, b. p. 115°/22 mm. The *aurichloride*, $C_{10}H_{19}ON,HAuCl_4$, was analysed. The *nitroso*-derivative, $C_{10}H_{18}ON{\cdot}NO$, crystallises in light spears, m. p. 51—52°.

1-*Nitroso*-6-*phenyl*-2 : 2-*dimethylpiperidone* (*nitrosobenzylidenediacetonamine*), $\mathrm{CO}<\begin{matrix}\mathrm{CH_2\cdot CHPh}\\ \mathrm{CH_2{-}CMe_2}\end{matrix}>\mathrm{N{\cdot}NO}$, forms large, yellow, rhombic crystals, [$a:b:c = 0{\cdot}6465:0{\cdot}7286:1$], m. p. 66—68°. G. Y.

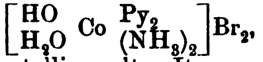
Hydroxoaquodipyridinediammincobalt and Diaquodipyridinediammincobalt Salts. ALFRED WERNER (*Ber.*, 1907, **40**, 468—479).—*Hydroxoaquodipyridinediammincobaltichloride*,



$$\left[\begin{matrix}\mathrm{HO}\\ \mathrm{H_2O}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{Py_2}\\ \mathrm{(NH_3)_2}\end{matrix}\right]\mathrm{Cl_2},$$

obtained by the addition of dichlorodiaquodiammincobaltichloride, $\left[\mathrm{Cl_2\ Co}\ \begin{matrix}\mathrm{(OH_2)_2}\\ \mathrm{(NH_3)_2}\end{matrix}\right]\mathrm{Cl}$, to a mixture of potassium chloride, water, and pyridine at 0°, separates as a pink, crystalline deposit with a nacreous lustre. Its aqueous solution is brownish-red, gives a feebly alkaline reaction with litmus, and quickly decomposes, the odour of pyridine becoming perceptible. When potassium bromide, potassium thiocyanate, &c. are added to a freshly-prepared solution, the corresponding hydroxoaquo-salts are precipitated.

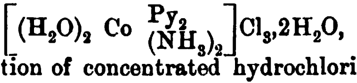
Hydroxoaquodipyridinediammincobaltibromide,



$$\left[\begin{matrix}\mathrm{HO}\\ \mathrm{H_2O}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{Py_2}\\ \mathrm{(NH_3)_2}\end{matrix}\right]\mathrm{Br_2},$$

is a violet-red, microcrystalline salt. It may also be obtained by the addition of potassium bromide to diaquodipyridinediammincobaltichloride by the treatment of the diaquo-bromide with water or by the precipitation of the aqueous solution with a little hydrobromic acid and by washing the diaquo-bromide with alcohol. The *nitrate* crystallises in bluish, pale-red needles; the *thiocyanate* forms violet-brown needles. The *dithionate* forms reddish-brown leaflets with a metallic lustre.

Diaquodipyridinediammincobaltichloride,



$$\left[\mathrm{(H_2O)_2\ Co}\ \begin{matrix}\mathrm{Py_2}\\ \mathrm{(NH_3)_2}\end{matrix}\right]\mathrm{Cl_3,2H_2O},$$

obtained by the action of concentrated hydrochloric acid on hydroxoaquodipyridinediammincobaltichloride, forms a grey, crystalline powder, and may be obtained also as ruby-red crystals or as greenish-grey or yellowish-brown prisms. When heated at 60°, it is converted into the *compound*, $\left[\mathrm{Cl_2\ Co}\ \begin{matrix}\mathrm{Py_2}\\ \mathrm{(NH_3)_2}\end{matrix}\right]\mathrm{Cl}$, which is a chocolate-coloured powder; its solution in water is brownish-red and gives an acid reaction.

When an aqueous solution of diaquodipyridinediammincobaltichloride is heated with concentrated hydrochloric acid, chlorine is evolved. When, however, concentrated hydrochloric acid is added to the solid salt, *dichlorodipyridinediammincobaltonitrate*,

$$\left[Cl_2\ Co\ \genfrac{}{}{0pt}{}{Py_2}{(NH_3)_2}\right]NO_3,$$

separates in dark green leaflets.

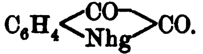
Diaquodipyridinediammincobaltibromide,

$$\left[(H_2O)_2\ Co\ \genfrac{}{}{0pt}{}{Py_2}{(NH_3)_2}\right]Br_3,2H_2O,$$

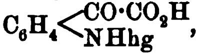
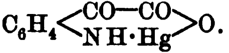
obtained by the action of concentrated hydrobromic acid on hydroxoaquodipyridinediammincobaltichloride, forms yellowish-brown leaflets. Its aqueous solution is brownish-red and shows an acid reaction. The *sulphate*, $\left[(H_2O)_2\ Co\ \genfrac{}{}{0pt}{}{Py_2}{(NH_3)_2}\right]_2(SO_4)_3,2H_2SO_4$, separates in brownish-violet leaflets. Its aqueous solution is red and shows an acid reaction. The *nitrate*, $\left[(H_2O)_2\ Co\ \genfrac{}{}{0pt}{}{Py_2}{(NH_3)_2}\right](NO_3)_3,2H_2O$, forms red crystals. The *dithionate*, $\left[(H_2O)_2\ Co\ \genfrac{}{}{0pt}{}{Py_2}{(NH_3)_2}\right]_2(S_2O_6)_3,2H_2O$, is a brown, crystalline powder. A. McK.

Mercury Salts of Isatin and of 1 : 3-Diketohydrindene. WALTER PETERS (*Ber.*, 1907, **40**, 235—240).—The author's aim is the preparation of *N*- and of *O*-metallic derivatives of isatin and of *C*- and *O*-derivatives of 1 : 3-diketohydrindene (compare Hantzsch, Abstr., 1902, i, 662).

Mercuryisatin, obtained in 95% yield by decomposing a boiling alcoholic solution of isatin with concentrated aqueous mercuric acetate, is a dark red, glistening substance which dissolves in alkalis to a yellow solution; consequently it has the constitution

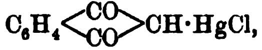


$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{Nhg}>CO.$$

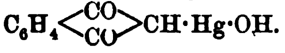
When an aqueous solution is treated with potassium hydroxide and subsequently neutralised, a precipitate of *o-mercuriaminobenzoylformic acid*,  $C_6H_4<\genfrac{}{}{0pt}{}{CO\cdot CO_2H}{NHhg}$, is obtained in glistening, white or grey leaflets containing $2H_2O$ which is lost at 100°, the substance turning red; at higher temperatures isatin is formed. An attempt to prepare the potassium salt of the preceding acid by passing carbon dioxide into an alkaline solution of mercury isatin, resulted in the formation of the *substance*,  $C_6H_4<\genfrac{}{}{0pt}{}{CO-CO}{NH\cdot Hg}>O$.

O-metallic derivatives of isatin have not been prepared.

When an aqueous or alcoholic solution of sodio-1 : 3-diketohydrindene is treated with excess of mercuric chloride, a light yellow *substance*,



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CH\cdot HgCl,$$

is obtained which is changed by sodium carbonate into a white *hydroxide*,  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>CH\cdot Hg\cdot OH$.

C. S.

Indolinones. KARL BRUNNER (*Monatsh.*, 1906, **27**, 1183—1192. Compare Abstr., 1897, i, 100; 1898, i, 90; 1905, i, 468; Schwarz, Abstr., 1903, i, 853).—A list is given of the indolinones which have been prepared by heating hydrazides with calcium oxide, and two new members of the group are described.

iso*Butyryl*-o-*tolylhydrazide*, $C_7H_7{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}CHMe_2$, formed by heating *o*-tolylhydrazine with *iso*butyric acid at 130°, crystallises in leaflets, m. p. 93°, and when heated with calcium oxide at 190—200° is converted into 3 : 3 : 7-*trimethylindoline*-2-*one*, $C_6H_8Me\Big\langle\substack{CMe_2\\NH}\Big\rangle CO$, which crystallises in colourless, rhombic leaflets, m. p. 150°, b. p. 285—295°, is soluble in concentrated mineral acids or aqueous alkalis, and gives a transient, intense, carmine-red coloration with manganese dioxide or potassium dichromate in concentrated sulphuric acid solution; the *silver* derivative, $C_{11}H_{12}ONAg$, forms microscopic prisms. The *bromo*-derivative, $C_{11}H_{12}ONBr$, formed by the action of hydrobromic acid on the indolinone, crystallises in rectangular leaflets, m. p. 179—180°.

iso*Butyryl*-p-*tolylhydrazide*, prepared from *iso*butyric acid and *p*-tolylhydrazine, crystallises in white leaflets, m. p. 147—148°, and when heated with calcium oxide at 220—240° yields 3 : 3 : 5-*trimethylindoline*-2-*one*, $C_{11}H_{18}ON$; this crystallises from dilute alcohol in leaflets, m. p. 144—145°, or in needles, m. p. 140° when rapidly heated, when slowly heated, m. p. 144—145°. It dissolves in hot concentrated sodium hydroxide and deposits the *sodium* derivative in long needles on cooling; the *silver* derivative, $C_{11}H_{12}ONAg$, is gelatinous. The *bromo*-derivative, $C_{11}H_{12}ONBr$, crystallises in long prisms, m. p. 214°.

G. Y.

A New Indolinol. GUIDO JENISCH (*Monatsh.*, 1906, **27**, 1223—1232).—Brunner (Abstr., 1898, i, 384, 682; 1900, i, 360) has shown that indolinium bases having an alkyl group in the position 2, lose water, forming 2-methyleneindolines, but that the ψ-ammonium base or indolinol is obtained if position 2 is occupied by hydrogen. This is now found to be the case with 2-arylindolinium bases.

2-*Phenyl*-1 : 3 : 3-*trimethyl*-2-*indolinol*, $C_6H_4\Big\langle\substack{CMe_2\\NMe}\Big\rangle CPh{\cdot}OH$, is formed by the successive action of alcoholic stannous chloride and potassium hydroxide on the condensation product of phenyl *iso*propyl ketone and *as*-phenylmethylhydrazine, or by the action of magnesium phenyl bromide on 1 : 3 : 3-trimethylindolinone in ethereal-benzene solution; it crystallises in almost colourless leaflets, m. p. 101—102°, and dissolves readily in dilute mineral acids, forming solutions which slowly became red on exposure to air. The *ferrichloride*,

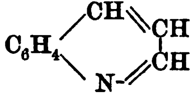
$C_{17}H_{18}NCl,FeCl_3$,

forms yellowish-green crystals; the *platinichloride*, $(C_{17}H_{18}NCl)_2PtCl_4$, m. p. 216—216·5°; the *picrate*, $C_{23}H_{22}O_8N_4$, m. p. 139—140°. The ψ-base remains unchanged when boiled with concentrated hydrochloric acid or heated with zinc chloride at 120°, but is oxidised by alcoholic potassium permanganate, and with hydrobromic acid in hydrochloric acid solution yields a crystalline *product*, m. p. 191°. G. Y.

Mechanism of the Synthesis of Quinoline Derivatives. Louis J. Simon (*Compt. rend.*, 1907, **144**, 138—140. Compare Abstr., 1906, i, 887, 888).—A theoretical paper discussing possible mechanisms of the synthesis of quinoline derivatives. E. H.

β-Chloroethyl Ketones and Alkyl Vinyl Ketones. Method of Synthesising 4-Alkylquinolines. Edmond E. Blaise and M. Maire (*Compt. rend.*, 1907, **144**, 93—95. Compare Abstr., 1906, i, 142).—4-Alkylquinolines can be readily prepared by heating 1 mol. of a β-chloroethyl ketone with 2 mols. of aniline in alcoholic solution on a water-bath, in this case the aniline hydrochloride, which is one of the products of the reactions, serves to effect the formation of a cyclic compound from the open chain compound first formed, and in fact β-anilinoethyl ethyl ketone yields the corresponding quinoline when heated with aniline hydrochloride. 4-*Ethylquinoline*, b. p. 134°/9 mm., yields cinchoninic acid on oxidation and differs from the compound described by Reher (Abstr., 1887, 279), which was probably impure; 4-n-*propylquinoline* has b. p. 159°/16 mm.

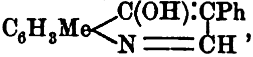
In view of the fact that phenolic amines form compounds with vinyl ketones owing to the presence of the ethylenic linking in the ketone, the authors suggest that Skraup's quinoline synthesis may be represented by the equations: $CH_2{:}CH{\cdot}CHO \longrightarrow NHPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}NPh$,

→  + NH_2Ph + H_2.

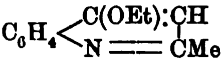
M. A. W.

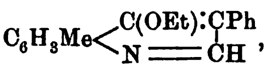
Alkylation of Pyridones. Hans Meyer (*Monatsh.*, 1906, **27**, 987—996. Compare Abstr., 1906, i, 108, 604).—The action of diazomethane on kynurine in ethereal solution in presence of a small quantity of methyl alcohol leads to the formation of 4-methoxyquinoline together with a small amount of the ψ-methyl ether. The *hydrochloride* of 4-methoxyquinoline crystallises in long, colourless needles, m. p. 164—166° (decomp.). *Kynurine aurichloride* forms slender, lemon-yellow needles, m. p. 217° (decomp.).

4-Methoxy-2-methylquinoline, formed by the action of diazomethane on 2-methylkynurine, crystallises in white needles, m. p. 62° (82°, Conrad and Limpach, Abstr., 1877, 679).

3-*Phenyl*-6-*methylkynurine*,  $C_6H_3Me<\begin{matrix}C(OH){:}CPh \\ N=\!=\!=CH\end{matrix}$, is prepared by the action of *p*-toluidine in presence of alcohol at the laboratory temperature on ethyl formylphenylacetate, obtained by treating ethyl phenylacetate with ethyl formate and sodium in ethereal solution, and heating the resulting ethyl α-phenyl-β-*p*-toluidinoacrylate at 300°. It crystallises from alcohol in long, white, glistening needles, m. p. 315°. When treated with a large excess of diazomethane it yields only a small amount of the O-*methyl ether*, $C_9H_4NPhMe{\cdot}OMe$, which separates from methyl alcohol in needles, m. p. 117°.

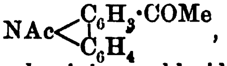
4-Methoxy-2-methyl- and 4-methoxy-3-phenyl-6-methylquinoline yield methyl iodide readily and quantitatively when heated with hydriodic acid; the corresponding 4-ethoxyquinolines have been prepared and their behaviour in this respect compared (see Goldschmiedt, this vol., i, 30).

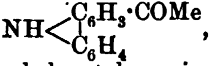
4-Ethoxy-2-methylquinoline,  $C_6H_4<\begin{matrix}C(OEt):CH\\ N{=\!=\!=}CMe\end{matrix}$, m. p. 40—41°, b. p. 290°, prepared by heating 4-chloro-2-methylquinoline (Conrad and Limpach, *loc. cit.*) with sodium ethoxide and absolute alcohol under pressure at 130°, reacts only slowly with hydriodic acid, and, when treated according to the Herzig-Meyer method of estimating *N*-alkyl groups, yields about 40% of the theoretical amount of silver iodide.

4-Chloro-3-phenyl-6-methylquinoline,  $C_6H_3Me<\begin{matrix}C(OEt):CPh\\ N{=\!=\!=}CH\end{matrix}$, prepared by the action of phosphorus pentachloride and oxychloride on the hydroxyquinoline, crystallises in white needles, m. p. 94°, and when heated with sodium ethoxide and absolute alcohol at 100° is converted into the O-*ethyl ether*; this is obtained as an oil, and yields ethyl iodide quantitatively when heated with hydriodic acid.

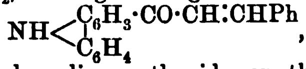
G. Y.

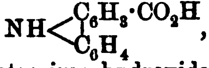
New Carbazoles. Walther Borsche and M. Feise (*Ber.*, 1907, 40, 378—386).—This investigation, undertaken with the object of preparing homologues of carbazole by the Friedel-Craft reaction, has led to the formation of carbazyl methyl ketones and by oxidation of these to that of carbazolecarboxylic acids. The position assumed by the acetyl- and carboxyl-groups respectively has not been determined. Attempts to do so were unsuccessful in consequence of the stability of 3-methylcarbazole (Delétra and Ullmann, Abstr., 1904, i, 270) towards oxidising agents. Two new formations of 3-methylcarbazole are described.

Diacetylcarbazole,  $NAc<\begin{matrix}C_6H_3\cdot COMe\\ |\\ C_6H_4\end{matrix}$, formed by the action of acetyl bromide and aluminium chloride on 9-acetylcarbazole in anhydrous carbon disulphide solution, is obtained as a brown, crystalline precipitate, m. p. 104°. The *oxime*, $C_{16}H_{14}O_2N_2$, crystallises from alcohol or ethyl acetate in white, nodular aggregates, m. p. 172°. Hydrolysis of the diacetyl compound with boiling alcoholic sulphuric acid leads to the formation of *carbazyl methyl ketone*,



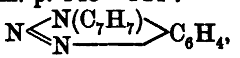
$$NH<\begin{matrix}C_6H_3\cdot COMe\\ |\\ C_6H_4\end{matrix},$$

which crystallises from alcohol or toluene in white leaflets, m. p. 227°; the *semicarbazone* crystallises in colourless scales, m. p. above 360°; the *oxime*, $C_{14}H_{12}ON_2$, forms glistening, colourless leaflets, m. p. 253°. *Cinnamoylcarbazole*,  $NH<\begin{matrix}C_6H_3\cdot CO\cdot CH:CHPh\\ |\\ C_6H_4\end{matrix}$, prepared by the action of benzaldehyde and sodium ethoxide on the methyl ketone in alcoholic solution, crystallises in small, yellow needles, m. p. 282°.

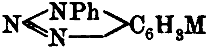
Carbazolecarboxylic acid,  $NH<\begin{matrix}C_6H_3\cdot CO_2H\\ |\\ C_6H_4\end{matrix}$, formed by heating the methyl ketone with fused potassium hydroxide, crystallises in slender, colourless needles, m. p. 320—322°; the *ethyl* ester, $C_{15}H_{13}O_2N$, forms colourless leaflets, m. p. 184°.

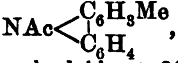
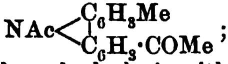
2′-Nitro-4-methyldiphenylamine (Jacobson and Lischke, Abstr., 1899, i, 276) is prepared by hydrolysis with concentrated hydrochloric acid in a sealed tube at 130—140° of *p*-toluidine 3-nitro-4-*p*-toluidinobenzenesulphonate formed by boiling *p*-toluidine 4-chloro-3-nitrobenzenesulphonate with *p*-toluidine.

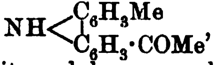
The benzoyl derivative of *p*-tolyl-*o*-phenylenediamine, $C_{20}H_{18}ON_2$, crystallises in colourless needles, m. p. 143—144°.

1-p-*Tolyl*-1 : 2 : 3-*benzotriazole*,  $N<\begin{matrix}N(C_7H_7)\\ N\end{matrix}>C_6H_4$, formed by the action of sodium nitrite on *p*-tolyl-*o*-phenylenediamine in hydrochloric acid solution, crystallises in colourless needles, m. p. 84—85°, and on distillation yields 3-methylcarbazole.

The *hydrochloride* of 2-amino-4-methyldiphenylamine, formed by the action of bromobenzene on nitrotoluidine in nitrobenzene solution and reduction of the resulting product, crystallises in colourless needles, m. p. 200—201°; the *base*, $NHPh{\cdot}C_6H_3Me{\cdot}NH_2$, crystallises in glistening needles, m. p. 140°. The *benzoyl* derivative, $C_{20}H_{18}ON_2$, crystallises from alcohol in colourless needles, m. p. 161°.

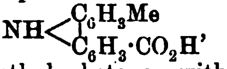
1-*Phenyl*-5-*methyl*-1 : 2 : 3-*benzotriazole*,  $N<\begin{matrix}NPh\\ N\end{matrix}>C_6H_3Me$, prepared by the action of nitrous acid on the preceding base, crystallises from a mixture of benzene and light petroleum in small, glistening prisms, m. p. 117°, and on distillation yields 3-methylcarbazole.

9-*Acetyl*-3-*methylcarbazole*,  $NAc<\begin{matrix}C_6H_3Me\\ |\\ C_6H_4\end{matrix}$, prepared by heating 3-methylcarbazole with acetic anhydride at 220—240°, is obtained as an oil which reacts with acetyl bromide and aluminium chloride, forming 9 *acetyl*-3-*methylcarbazyl methyl ketone*,  $NAc<\begin{matrix}C_6H_3Me\\ |\\ C_6H_3{\cdot}COMe\end{matrix}$; this crystallises in yellow needles, m. p. 131°, and on hydrolysis with sulphuric acid yields 3-*methylcarbazyl methyl ketone*,



$$NH<\begin{matrix}C_6H_3Me\\ |\\ C_6H_3{\cdot}COMe\end{matrix}$$

which crystallises in white nodules, m. p. about 200°.

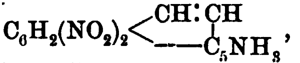
3-*Methylcarbazolecarboxylic acid*,  $NH<\begin{matrix}C_6H_3Me\\ |\\ C_6H_3{\cdot}CO_2H\end{matrix}$, formed by fusing 9-acetyl-3-methylcarbazyl methyl ketone with potassium hydroxide, crystallises in colourless scales, which darken above 220°, m. p. 265°.
G. Y.

Estimation of Loosely Combined Methylene Groups.

Emil Votoček and Viktor Veselý (*Ber.*, 1907, **40**, 410—414).—Methylene derivatives which contain the methylene group attached to oxygen of aliphatic compounds or those containing the methylene groups attached to nitrogen readily react with a glacial acetic acid solution of carbazole in the presence of hydrochloric or sulphuric acid, yielding insoluble products. It is claimed that the compound, m. p. 202—203°, obtained by Morgan (Trans., 1898, **73**, 550) by the action of formaldehyde on β-naphthylamine cannot have the constitution suggested, as it does not react with carbazole. The product obtained by the action of formaldehyde on carbazole has the composition $C_{20}H_{20}ON_2$.

Carbazole and dimethylene gluconic acid yields a crystalline product, $C_{25}H_{18}N_2$ m. p., above 280°. J. J. S.

Nitro-derivatives of β-Naphthaquinoline. Hans Hepner (*Monatsh*, 1906, **27**, 1045—1068. Compare Haid, Abstr., 1906, i, 605; Claus and Besseler, Abstr., 1898, i, 331).—On nitration at 70—80° by Claus and Kramer's method (Abstr., 1885, 908), β-naphthaquinoline yields a dinitro-derivative,



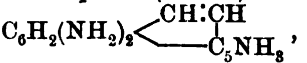
$$C_6H_2(NO_2)_2<\begin{matrix}CH:CH\\ \quad\;|\\ \quad C_5NH_3\end{matrix},$$

which forms microscopic needles, m. p. 249°; when recrystallised from concentrated hydrochloric acid it forms a *hydrochloride*,

$$C_{13}H_7N(NO_2)_2,HCl,$$

which crystallises in prismatic needles, m. p. 249°, evolving hydrogen chloride, and decomposes on treatment with water.

Nitration of β-naphthaquinoline at the laboratory temperature leads to the formation of a mononitro-derivative, m. p. 173°, which is identical with Claus and Besseler's compound (*loc. cit.*).

Diamino-β-naphthaquinoline,  $C_6H_2(NH_2)_2<\begin{matrix}CH:CH\\ \quad\;|\\ \quad C_5NH_3\end{matrix}$, prepared reduction of the dinitro-compound with stannous chloride and hydrochloric acid, crystallises in yellow, microscopic needles, m. p. 249°; the *hydrochloride*, $C_{13}H_7N(NH_2)_2,2HCl$, forms dark red needles, remains unchanged at 300°, but at higher temperatures decomposes without melting, and when recrystallised from concentrated hydrochloric acid forms an unstable *trihydrochloride*; the *sulphate*,

$$C_{13}H_7N(NH_2)_2,H_2SO_4,H_2O;$$

nitrate, $C_{13}H_7N(NH_2)_2,2HNO_3$, and *stannochloride*,

$$C_{13}H_7N(NH_2)_2,2HCl,2SnCl_2,$$

are described. On oxidation with potassium permanganate or chromic acid in sulphuric acid solution, the base yields *quinoline-5 : 6-dicarboxylic acid*, $C_9H_5N(CO_2H)_2,H_2O$, which crystallises in almost colourless, rhombic leaflets, sinters at 233°, m. p. 238—241° (decomp.), and is stable towards oxidising agents. A number of salts are described; the *lead*, $C_9H_5N(CO_2H)_2Pb,\frac{1}{2}H_2O$, and *basic copper*,

$$C_9H_5N(CO_2H)_2Cu,Cu(OH)_2,H_2O,$$

salts were analysed. The *hydrochloride*, $C_9H_5N(CO_2H)_2,HCl$, forms strongly refracting, colourless prisms; the *nitrate*,

$$C_9H_5N(CO_2H)_2,HNO_3,H_2O,$$

crystallises in needles, m. p. 208—210° (decomp.); the *platinichloride*, $[C_9H_5N(CO_2H)_2]_2,H_2PtCl_6$, forms yellow needles and gradually decomposes when heated. G. Y.

Constitution of *o*-Tolidine. Gustav Schultz, Georg Rohde, and F. Vicari (*Annalen*, 1907, **352**, 111—131. Compare Abstr., 1904, i, 532).—Proof is given that *o*-tolidine is 4 : 4′-diamino-3 : 3′-

dimethyldiphenyl. *Sodium bisdiazo-*o*-ditolylsulphonate* is obtained by adding sodium sulphite to a cold diazotised solution of *o*-tolidine in sulphuric acid; it crystallises in white needles which when heated decompose without melting.

This substance when reduced by stannous chloride and hydrochloric acid is converted into o*-tolidinedihydrazine hydrochloride*, which crystallises in yellow needles; the *free base* is obtained as a greyish-white precipitate by decomposing the hydrochloride with sodium carbonate or sulphite; it could not be obtained in a crystalline form; by warming it with an alcoholic solution of benzaldehyde, a yellow substance is obtained; with acetone a grey *substance* is obtained. By distilling a mixture of *o*-tolidinedihydrazine with copper acetate, 3 : 3′-dimethyldiphenyl, $C_{14}H_{14}$, is obtained; it is a colourless oil, b. p. 286—287°/713 mm., which solidifies at $-16°$ to a white, crystalline mass, m. p. $+5$—7°. The same compound is obtained by the action of sodium on *m*-iodotoluene in ether, therefore in *o*-tolidine the methyl groups occupy the 3 : 3′-positions.

3 : 3′-Dimethyldiphenyl is converted by a mixture of nitric and sulphuric acids into 4 : 4′-dinitro-3 : 3′-dimethyldiphenyl, $C_{14}H_{12}O_4N_2$, which crystallises in faintly yellow needles, m. p. 228°. When reduced with sodium sulphide it is converted into 4-nitro-4′-amino-3 : 3′-dimethyldiphenyl which crystallises in yellow needles, m. p. 142—143°; *o*-tolidine is obtained from the latter compound by reduction with tin and hydrochloric acid in alcoholic solution.

That in *o*-tolidine the amino-groups occupy the 4 : 4′-positions is shown by the fact that the same dichlorodiphenyldicarboxylic acid is obtained both from *o*-tolidine and from benzidinedicarboxylic acid. In the latter substance the 4 : 4′-positions of the amino-groups has been definitely proved.

Dichloro-3 : 3′-dimethyldiphenyl, obtained by Sandmeyer's reaction from *o*-tolidine, may be oxidised to dichlorodiphenyldicarboxylic acid; the acid has m. p. 323—324° and its methyl ester, m. p. 134°. When heated above 324°, carbon dioxide is evolved and 4 : 4′-dichlorodiphenyl is formed. W. H. G.

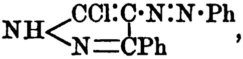
Hydroxy-derivatives of Malachite-Green. EMIL VOTOČEK and J. JELÍNEK (*Ber.*, 1907, **40**, 406—410. Compare Noelting and Gerlinger, Abstr., 1906, i, 610).—o*-Methoxyleucomalachite-green*, $C_{24}H_{28}ON_2$, obtained from anisaldehyde and dimethylaniline, crystallises from alcohol in colourless prisms, m. p. 106°, and when oxidised yields a green dye with a red fluorescence. The corresponding *ethoxy*-derivative melts at 125° and also yields a green dye. The *leuco-base*, $C_{24}H_{26}O_2N_2$, from piperonal and dimethylaniline melts at 109—110° and yields a bluish-green dye. Anisole and tetramethyldiaminobenzhydrol yield a *leuco-base*, $C_{24}H_{28}ON_2$, m. p. 155°, which is oxidised to a blue dye. It dyes cotton mordanted with tannin a greenish-blue, but this changes to violet on the addition of alkalis. The corresponding *leuco-base* from phenetole melts at 165° and yields a dye which gives a blue colour on mordanted cotton. The addition of alkali produces a violet colour. Guaiacol and tetramethyldiaminobenzhydrol yield a *leuco-base* which forms pale rose-coloured crystals, m. p.

134—135°. The corresponding dye is blue. β-Naphthol and tetramethyldiaminobenzhydrol yield a leuco-base which could not be isolated in a crystalline form. The corresponding dye is pure blue in colour. The *acetyl* derivative of the leuco-base, $C_{29}H_{30}O_2N_2$, melts at 136° and yields a green dye. J. J. S.

3-Phenyl-1-methyl-5-pyrazolone. AUGUST MICHAELIS (*Annalen*, 1907, **352**, 152—217).—Although 1-phenyl-3-methyl-5-pyrazolone and its derivatives have been studied extensively, the isomeric 3-phenyl-1-methyl-5-pyrazolone had not been investigated to any extent. The two isomerides, although different physically, are very similar chemically, differing chiefly in their behaviour towards benzaldehyde, with which substance 1-phenyl-3-methyl-5-pyrazolone alone gives a crystalline benzylidene derivative. From 3-phenyl-1-methyl-5-pyrazolone an antipyrine has been prepared which the author calls *iso*antipyrine, the isomeride previously known by this name being called 3-antipyrine; all three isomeric antipyrines behave similarly physiologically, the 3-antipyrine being the most poisonous.

[With WILHELM RASSMANN.]—By heating 3-phenyl-5-pyrazolone, dissolved in benzene, with phosphorus oxychloride in sealed tubes at 190—200°, 5-*chloro*-3-*phenylpyrazole* is formed; it crystallises in white needles, m. p. 142°, but sublimes below this temperature, and distils undecomposed at 295°/760 mm.; soluble both in strong acids and dilute alkalis; the *silver* salt, $C_9H_6N_2ClAg$, and *hydrochloride*, $C_9H_7N_2Cl,HCl$, m. p. 131°, decomposed by water into its components, have been prepared. 5-Chloro-3-phenylpyrazole when heated with phosphorus pentachloride in sealed tubes at 120° is converted into 4:5-*dichloro*-3-*phenylpyrazole*, m. p. 95—96°, whilst with bromine in acetic acid solution it gives 5-*chloro*-4-*bromo*-3-*phenylpyrazole*, which crystallises in white needles, m. p. 90°.

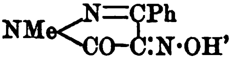
4-*Benzeneazo*-5-*chloro*-3-*phenylpyrazole*,



$NH<\begin{matrix}CCl:C\cdot N:N\cdot Ph\\ N{=}CPh\end{matrix}$

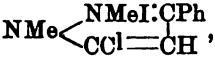
, cannot be directly obtained from 5-chloro-3-phenylpyrazole; it is prepared by acting on 4-benzeneazo-3-phenyl-5-pyrazolone with phosphorus oxychloride and crystallises in red needles, m. p. 192°; the chlorine atom cannot be replaced by hydrogen, as is possible with other benzeneazochloropyrazoles. By acting on 5-chloro-3-phenylpyrazole with a mixture of nitric and sulphuric acids, 5-*chloro*-3-*nitrophenylpyrazole* is obtained; it crystallises in yellowish-green needles, m. p. 180°; that the nitro-group is present in the phenyl radicle is shown by the fact that on brominating this compound, 5-*chloro*-4-*bromo*-3-*nitrophenylpyrazole*, yellow needles, m. p. 130°, is formed, the same compound being obtained by nitrating 5-chloro-4-bromo-3-phenylpyrazole.

[With HUGO DORN.]—A better yield of 3-phenyl-1-methyl-5-pyrazolone is obtained from 3-phenyl-5-pyrazolone by using methyl sulphate instead of methyl iodide (compare von Rothenburg, Abstr., 1895, i, 686); that the compound has the formula assigned to it is supported by the fact that it is obtained by the condensation of methylhydrazine with ethyl benzoylacetate; further, since its *iso*nitroso-derivative is red, it is undoubtedly a 5-pyrazolone, the nitroso-derivatives of 3-pyrazolones being green. The following salts have been obtained in a crystalline form: *hydrochloride*, $C_{10}H_{10}ON_2,HCl,H_2O$; *sulphate*, $C_{10}H_{10}ON_2,H_2SO_4,2H_2O$, and *nitrate*, $C_{10}H_{10}ON_2,HNO_3,H_2O$. On treatment with nitrous acid, 3-phenyl-1-methyl-5-pyrazolone is converted into 4-iso*nitroso*-3-*phenyl*-1-*methyl*-5-*pyrazolone*,



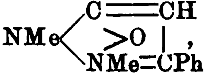
$NMe<\begin{matrix}N{=}CPh\\ CO{-}C{:}N{\cdot}OH\end{matrix}$, crystallising in orange leaflets, m. p. 162°; it dissolves in alkalis and gives the Liebermann's reaction.

4-*Benzeneazo*-3-*phenyl*-1-*methyl*-5-*pyrazolone* is produced by the interaction of 3-phenyl-1-methyl-5-pyrazolone with diazobenzene chloride; it forms orange needles, m. p. 158°; when heated with phosphorus oxychloride in sealed tubes at 120° it is converted into 4-*benzeneazo*-5-*chloro*-1-*methyl*-3-*phenylpyrazole*, which forms yellow needles, m. p. 94°; the chlorine cannot be replaced by hydrogen by the action of tin and hydrochloric acid. When 3-phenyl-1-methyl-5-pyrazolone is heated with phosphorus oxychloride at 160° it is converted into 5-*chloro*-3-*phenyl*-1-*methylpyrazole*, which is obtained also by heating 5-chloro-3-phenylpyrazole with methyl iodide in sealed tubes at 100°; it crystallises in white leaflets, m. p. 62°. When heated with excess of methyl iodide for several days, the *methiodide*,



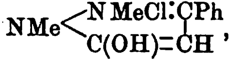
$NMe<\begin{matrix}NMeI{:}CPh\\ CCl{=}CH\end{matrix}$, forming colourless needles, m. p. 167°, is obtained together with a *periodide*, $C_{11}H_{12}N_2ClI,I_4$, which forms dark reddish-violet leaflets, m. p. 105°; the periodide is also formed by adding iodine to the methyl iodide derivative; the *hydrochloride*, $C_{10}H_9N_2Cl,HCl$, m. p. 95°, and *platinichloride*, $(C_{10}H_9N_2Cl)_2H_2PtCl_6,2H_2O$, m. p. 193°, were prepared. An isomeric 3-*chloro*-5-*phenyl*-1-*methylpyrazole* is obtained either by methylating 5-chloro-3-phenylpyrazole in alcoholic solution or by eliminating methyl chloride from antipyrine chloride by the action of phosphorus oxychloride; it crystallises in white needles, m. p. 76°. When heated with potassium hydrogen sulphide, the methyl iodide derivatives of either of these isomerides give the same thiopyrine, and with alkalis they yield the same antipyrine. The formula given to the compound has not been definitely proved. When heated with phosphorus pentachloride in sealed tubes at 140°, or treated in acetic acid solution with bromine, 5-chloro-3-phenyl-1-methylpyrazole is converted respectively into 4:5-*dichloro*-3-*phenyl*-1-*methylpyrazole*, which forms transparent crystals, m. p. 25·5°, b. p. 317°/760 mm., and 5-*chloro*-4-*bromo*-3-*phenyl*-1-*methylpyrazole*, white needles, m. p. 65°. A *perbromide*, $C_{10}H_8N_2ClBr_3$, is obtained by adding excess of bromine to a solution of 5-chloro-3-phenyl-1-methylpyrazole in light petroleum; it is a yellow powder, m. p. 103°, and is converted by sodium hydroxide into the preceding compound, m. p. 65°. Iodine in the presence of iodic acid converts 5-chloro-3-phenyl-1-methylpyrazole into 5-*chloro*-4-*iodo*-3-*phenyl*-1-*methylpyrazole*, white needles, m. p. 105°.

iso*Antipyrine* (2 : 5-*oxy*-3-*phenyl*-1 : 2-*dimethylpyrazole*),



$$\mathrm{NMe}\!<\!\begin{matrix}\mathrm{C{=\!=}CH}\\ {>}\mathrm{O}\ \ |\\ \mathrm{NMe{=}CPh}\end{matrix},$$

may be prepared, either by heating 3-phenyl-1-methyl-5-pyrazolone (1 mol.) with methyl iodide (1 mol.) in a sealed tube at 100° or from 3-phenyl-5-pyrazolone by heating with methyl iodide; it forms white crystals, which soften at 98° and completely liquefy at 108°, and differs from Knorr's antipyrine in that it is hygroscopic and gives with mercuric chloride a precipitate which dissolves only with great difficulty on heating, whereas with antipyrine the precipitate dissolves immediately on warming slightly. The following salts of *iso*antipyrine have been prepared; the *hydrochloride*,



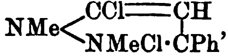
$$\mathrm{NMe}\!<\!\begin{matrix}\mathrm{NMeCl{:}CPh}\\ |\\ \mathrm{C(OH){=}CH}\end{matrix},$$

white needles, m. p. 207°; *hydroiodide*, $C_{11}H_{12}ON_2,HI,H_2O$, crystalline powder, m. p. 100—118° (decomp.); *hydroferrocyanide*, $(C_{11}H_{12}ON_2)_2,H_4Fe(CN)_6$, yellowish-white powder; *hydroferricyanide*, yellow needles, m. p. 122° (decomp.); *picrate*, $C_{11}H_{12}ON_2,C_6H_3O_7N_3$, yellow needles, m. p. 142°.

When *iso*antipyrine is treated with bromine in chloroform, a *perbromide*, m. p. 187° (decomp.), is formed; the latter on treatment with water gives rise to 4-*bromo*iso*antipyrine*, crystallising in white leaflets, m. p. 179°; by the action of nitrous acid, *iso*antipyrine is converted into 4-*nitroso*-iso*antipyrine*, which crystallises in emerald-green leaflets, m. p. 215° (decomp.); it is decomposed by warm sodium hydroxide; its *hydrochloride*, $C_{11}H_{11}O_2N_3,HCl$, crystallises in orange needles, m. p. 162°; by treating *iso*antipyrine in strong hydrochloric acid with an excess of sodium nitrite it is converted into 4-*nitro*iso*antipyrine*, crystallising in yellow prisms, m. p. 143° (decomp.).

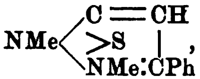
4 : 4′-*Benzylidenedi*-iso*antipyrine*, $CHPh(C_8N_2PhMe_2O)_2$, is produced by the condensation of *iso*antipyrine (2 mols.) with benzaldehyde (1 mol.) in the presence of a little strong hydrochloric acid; it crystallises in white leaflets containing $2H_2O$; m. p. 70° when hydrated or 213° when anhydrous, it gives no coloration with ferric chloride.

5-*Chloro*-3-*phenyl*-1-*methylpyrazole* ("iso*Antipyrine chloride*"),



$$\mathrm{NMe}\!<\!\begin{matrix}\mathrm{CCl{=\!=}CH}\\ |\\ \mathrm{NMeCl{\cdot}CPh}\end{matrix},$$

obtained by the action of phosphorus oxychloride on *iso*antipyrine, is a white, hygroscopic powder containing, when precipitated from alcoholic solution by ether, $2H_2O$, m. p. 70°, or when anhydrous, m. p. 130°; it gives a faint red coloration with ferric chloride, and when heated decomposes into 3-chloro-5-phenyl-1-methylpyrazole and methyl chloride; when treated with picric acid in alcoholic solution, the 2-chlorine atom is replaced, the *compound* formed, $C_{11}H_{12}N_2Cl{\cdot}O{\cdot}C_6H_2(NO_2)_3$, crystallises in yellow leaflets, m. p. 155°; the same chlorine atom of *iso*antipyrine chloride may be replaced by iodine by treatment with potassium iodide; the *platinichloride*, $(C_{10}H_9N_2CH_3Cl)_2PtCl_6,2H_2O$, m. p. 214°; and *mercurichloride*, $C_{11}H_{12}N_2Cl_2,HgCl_2$, m. p. 136°, are crystalline.

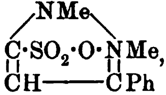
isoThiopyrine,  $\mathrm{NMe}<\begin{array}{l}\mathrm{C{=}CH}\\ \;>\mathrm{S}\quad|\\ \mathrm{NMe{:}CPh}\end{array}$, is obtained by treating "*iso*antipyrine chloride" with potassium hydrogen sulphide; it crystallises in long needles, m. p. 178°, and is coloured yellow by sulphurous acid; on one occasion an *isomeride*, m. p. 162°, of similar properties was obtained, but could not again be prepared. The *hydrochloride*,

$$C_{11}H_{12}N_2S,HCl,$$

crystallises in needles, m. p. 155—162°; the *platinichloride*,

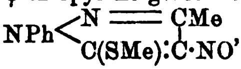
$$(C_{11}H_{12}N_2S)_2,H_2PtCl_6,2H_2O,$$

is a red powder, m. p. 231°; *mercurichloride*, $C_{11}H_{12}N_2S,HgCl_2$, a white, crystalline powder, m. p. 224°; *hydroiodide*, $C_{11}H_{12}N_2S,HI$, forms monoclinic crystals, m. p. 131°; the *methiodide*, $C_{11}H_{12}N_2S,MeI,H_2O$, crystallises in needles, m. p. 102·5°.

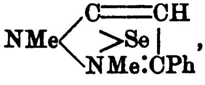
isoThiopyrine trioxide,  $\begin{array}{c}\mathrm{NMe}\\ \mathrm{C{\cdot}SO_2{\cdot}O{\cdot}NMe}\\ \mathrm{CH{-\!-\!-}CPh}\end{array}$, prepared by heating "*iso*antipyrine chloride" with a solution of sodium sulphite, forms fan-shaped crystals, m. p. 291°.

ψ-iso*Thiopyrine* (5-*methylthiol*-3-*phenyl*-1-*methylpyrazole*) is obtained by distilling the methyl iodide derivative of *iso*thiopyrine; it is a colourless liquid, b. p. 184°/10 mm., and combines with methyl iodide at 100°, forming the compound from which it is prepared; its *hydrochloride*, $C_{11}H_{12}N_2S,HCl,H_2O$, forms white needles, m. p. 106°, or when anhydrous, m. p. 158°; *platinichloride*,

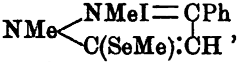
$$(C_{11}H_{12}N_2S)_2,H_2PtCl_6,H_2O,$$

yellow needles, m. p. 204°; *hydroiodide*, $C_{11}H_{12}N_2S,HI,H_2O$, m. p. 174°. When ψ-*iso*thiopyrine is acted on by nitrous acid, 4-*nitroso*-ψ-iso*thiopyrine* is formed; it crystallises in green needles, m. p. 137°. The isomeric ψ-thiopyrine gives under the same conditions 4-*nitroso*-ψ-*thiopyrine*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{C(SMe){:}C{\cdot}NO}\end{array}$, which forms dark green leaflets, m. p. 96°.

[With Thomas von der Hagen.]—iso*Selenopyrine*,

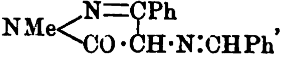


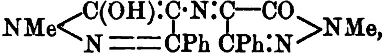
$$\mathrm{NMe}<\begin{array}{l}\mathrm{C{=}CH}\\ \;>\mathrm{Se}\;|\\ \mathrm{NMe{:}CPh}\end{array},$$

is formed by the interaction of "*iso*antipyrine chloride" with potassium hydrogen selenide; it crystallises in white needles, m. p. 198°, and gives no coloration with ferric chloride, but with sulphurous acid a temporary yellow coloration is produced; it does not readily form salts with acids, crystallising unchanged from hydrochloric acid; the *platinichloride* is a brown powder which commences to decompose at 150° and does not melt at 300°; the *mercurichloride* is a white powder, m. p. 200° (decomp.); the *methiodide*,  $\mathrm{NMe}<\begin{array}{l}\mathrm{NMeI{=}CPh}\\ \mathrm{C(SeMe){:}CH}\end{array}$, crystallises with $8H_2O$, m. p. 152°; the corresponding *ethiodide*, $C_{11}H_{12}N_2Se,EtI$, forms anhydrous crystals, m. p. 118°.

*Dichloro*iso*selenopyrine*, $C_{11}H_{12}N_2Cl_2Se$, is formed by passing chlorine into a chloroform solution of *iso*selenopyrine; it is a light yellow powder, m. p. 163° (decomp.). By the action of bromine, iso*selenopyrine tetrabromide*, $C_{11}H_{12}N_2Br_4Se$, is obtained in golden-brown needles, m. p. 108°; when repeatedly evaporated with water it is converted into iso*selenopyrine dibromide*, $C_{11}H_{12}N_2BrSe_2$, which forms golden-yellow needles, m. p. 215°, and on treatment with sodium carbonate is converted into *iso*selenopyrine.

iso-*ψ-Selenopyrine* (5-*methylselenol*-3-*phenyl*-1-*methylpyrazole*) is formed by the combination of methyl iodide with *iso*selenopyrine in ether; it is a light yellow liquid, b. p. 196—197°/15 mm.; it combines with chlorine to form a *dichloride*, a yellowish-green powder, m. p. 161°; the *dibromide*, m. p. 177°, when heated with a solution of sodium carbonate is converted into 4-*bromo*iso-*ψ-selenopyrine*, m. p. 129°; the *hydrochloride* of *iso-ψ*-selenopyrine, $C_{11}H_{12}N_2Se,HCl$, forms white needles, m. p. 106°; the *platinichloride*, $(C_{11}H_{12}N_2Se)_2,H_2PtCl_6$, is a reddish-brown powder, and does not melt at 300°. On treatment with nitrous acid, *iso-ψ*-selenopyrine gives 4-*nitroso*iso-*ψ-thiopyrine*, which crystallises in green needles, m. p. 136°.

[With Hans Wrede.]—By the reduction of 4-*iso*nitroso-3-phenyl-1-methyl-5-pyrazolone with zinc dust in acetic acid solution, 4-*amino*-3-*phenyl*-1-*methyl*-5-*pyrazolone* is produced; it cannot be obtained in the free state since it at once oxidises to *iso*rubazonic acid; its *hydrochloride* forms white needles, m. p. 175° (decomp.). The base condenses readily with aldehydes; the *benzylidene* derivative,  $\mathrm{NMe}<\begin{array}{l}\mathrm{N{=}CPh}\\ \mathrm{CO\cdot CH\cdot N{:}CHPh}\end{array}$, crystallises in yellow needles, m. p. 227°; the o-*hydroxybenzylidene* derivative, $C_{10}H_9ON_2\cdot N{:}CH\cdot C_6H_4\cdot OH$, crystallises in faintly yellow prisms, decomposing at 230°; the p-*methoxybenzylidene* derivative crystallises in yellow needles, m. p. 220° (decomp.), and the p-*nitrobenzylidene* derivative commences to decompose at 250°; *furfurylidene* and *cinnamylidene* derivatives melt at 180° and 152° respectively.

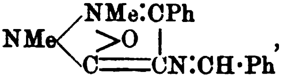
iso*Rubazonic acid*,  $\mathrm{NMe}<\begin{array}{l}\mathrm{C(OH){:}C\cdot N{:}C—CO}\\ \mathrm{N{=\!=}CPh\ \ CPh{:}N}\end{array}>\mathrm{NMe}$, is obtained by the oxidation of 4-amino-3-phenyl-1-methyl-5-pyrazolone with ferric chloride; it crystallises in dark red needles, m. p. 188°; it forms violet-coloured salts with alkalis; treatment with phenylhydrazine gives benzeneazo-3-phenyl-1-methyl-5-pyrazolone.

4-*Amino*iso*antipyrine*, $C_{11}H_{13}ON_3$, is obtained by the reduction of 4-nitroso*iso*antipyrine with zinc dust and acetic acid or stannous chloride and hydrochloric acid; it forms large, white, stable crystals, m. p. 109°; the *hydrochloride*, $C_{11}H_{13}ON_3,HCl$, crystallises in white needles, m. p. 210°; the *stannochloride*, $(C_{11}H_{13}ON_3)_2,SnCl_2$, forms thick, white crystals which are decomposed by hydrochloric acid when concentrated with the precipitation of 4-amino*iso*antipyrine hydrochloride; the *sulphate*, $C_{11}H_{13}ON_3,H_2SO_4$, m. p. 205°, and *picrate*,

$$C_{11}H_{13}ON_3,C_6H_2(NO_2)_3\cdot OH,$$

yellow prisms decomposing at 165° were also prepared. *Amino*iso*antipyrine mucobromate*, $C_{11}H_{13}ON_3,C_4H_2O_3Br_2$, is a yellow powder, m. p. 115°, obtained by mixing together solutions of its components.

The following condensation products of 4-amino*iso*antipyrine with various aldehydes and ketones were prepared.

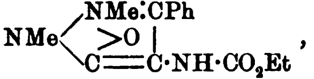
*Benzylideneamino*iso*antipyrine*,


$$\mathrm{NMe}\left\langle\begin{array}{l}\mathrm{NMe{:}CPh}\\ \quad >\mathrm{O}\ \ |\\ \mathrm{C{=\!=}CN{:}CH{\cdot}Ph}\end{array}\right.$$

, crystallises in yellow prisms, m. p. 151°; o-*hydroxybenzylideneamino*iso*antipyrine*, yellow needles, m. p. 173°; p-*methoxybenzylideneamino*iso*antipyrine*, yellow needles, m. p. 177°; p-*nitrobenzylidene* derivative, m. p. 155°; *cinnamylidene* derivative, colourless prisms, m. p. 151°; *ethyl acetoacetate* derivative, colourless crystals, m. p. 141°, and *acetophenone* derivative, colourless prisms, m. p. 167°.

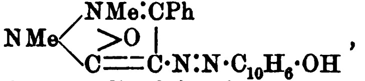
*Formylamino*iso*antipyrine*, $C_{11}H_{11}ON_2{\cdot}NH{\cdot}COH$, crystallises in colourless, rhombic plates, m. p. 209°; *acetylamino*iso*antipyrine* forms colourless prisms, m. p. 233°; *benzoylamino*iso*antipyrine* crystallises in colourless crystals, m. p. 234°; a dibenzoyl derivative could not be prepared. *Benzenesulphonylamino*iso*antipyrine*, $C_{11}H_{11}ON_2{\cdot}NH{\cdot}SO_2Ph$, crystallises in needles, m. p. 245°.

s-*Di*-iso*antipyrylthiocarbamide*, $CS(NH{\cdot}C_3N_2Me_2PhO)_2$, obtained by heating amino*iso*antipyrine in alcoholic solution with carbon disulphide, crystallises in white prisms, m. p. 225°. By heating 4-amino*iso*antipyrine with phenylthiocarbimide in alcoholic solution, *phenyl*iso*antipyrylthiocarbamide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}C_{11}H_{11}ON_2$, is obtained, crystallising in white needles, m. p. 210°. iso*Antipyrylurethane*,



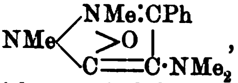
$$\mathrm{NMe}\left\langle\begin{array}{l}\mathrm{NMe{:}CPh}\\ \quad >\mathrm{O}\ \ |\\ \mathrm{C{=\!=}C{\cdot}NH{\cdot}CO_2Et}\end{array}\right.,$$

forms colourless crystals, m. p. 190°. Although the diazo-derivatives of pyrazoles and pyrazolones are stable, no diazo-derivative of amino*iso*antipyrine could be isolated; however, a freshly-diazotised solution of amino*iso*antipyrine gives with β-naphthol the *dye*,



$$\mathrm{NMe}\left\langle\begin{array}{l}\mathrm{NMe{:}CPh}\\ \quad >\mathrm{O}\ \ |\\ \mathrm{C{=\!=}C{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH}\end{array}\right.,$$

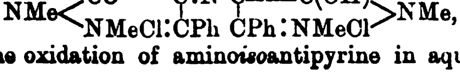
a red, crystalline substance dissolving in concentrated sulphuric acid with a violet colour.

*Dimethylamino*iso*antipyrine* (iso*pyramidone*),


$$\mathrm{NMe}\left\langle\begin{array}{l}\mathrm{NMe{:}CPh}\\ \quad >\mathrm{O}\ \ |\\ \mathrm{C{=\!=}C{\cdot}NMe_2}\end{array}\right.$$

, is prepared by acting on aminoantipyrine with either methyl iodide or methyl sulphate; it forms monoclinic crystals, m. p. 118°; the *picrate*, $C_{13}H_{17}ON_3,C_6H_2(NO_2)_3{\cdot}OH$, crystallises in yellow leaflets, m. p. 166°; the *methiodide* forms colourless needles, m. p. 197°. *Diethylamino*iso*antipyrine*, obtained by acting on amino*iso*antipyrine with ethyl sulphate, is a colourless oil. By heating amino*iso*antipyrine with ethylene bromide at 140°, both *di*-iso*antipyrinediethylenediamine*, $C_4H_8N_2(C_{11}H_{11}ON_2)_2$, white crystals, m. p. 300°, and *di*-iso*antipyrineethylenediamine*, $C_2H_4N_2(C_{11}H_{11}ON_2)_2$, white needles, m. p. 132°, are obtained; the *picrate* of the latter crystallises in yellow needles, m. p. 148°.

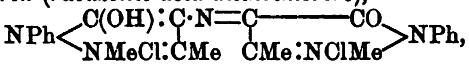
iso*Antipyrine-red* (iso*rubazonic acid methochloride*),



$$\mathrm{NMe}\!<\!\begin{array}{l}\mathrm{CO{-\!-}C{:}N{\cdot}C{=\!=}C(OH)}\\ \mathrm{NMeCl{:}CPh\ \ CPh{:}NMeCl}\end{array}\!>\!\mathrm{NMe},$$

is formed by the oxidation of amino*iso*antipyrine in aqueous solution with ferric chloride and the subsequent addition of concentrated hydrochloric acid; it crystallises in red needles, m. p. 207°, and dissolves readily in water, forming red solutions; the colour of the solution is destroyed by reducing agents and alkalis; strong alkalis precipitate from concentrated solutions of the substance a yellow crystalline powder, m. p. 159°, which seems to be *di*-iso*antipyrylamine*, $NH(C_{11}H_{11}ON_2)_2$; the *hydrochloride* of this base is therefore the leuco-base of *iso*antipyrine-red, into which substance it is converted by oxidising agents.

Antipyrine-red (*rubazonic acid methochloride*),



$$\mathrm{NPh}\begin{array}{l}\diagup\mathrm{C(OH)\!:\!C\cdot N{=}C\text{———————}CO}\diagdown\\ \diagdown\mathrm{NMeCl\!:\!CMe\quad CMe\!:\!NClMe}\diagup\end{array}\mathrm{NPh},$$

m. p. 215°, is obtained in similar manner from aminoantipyrine; it closely resembles *iso*antipyrine-red; its violet solution in water gives with strong sodium hydroxide, *diantipyrylamine*, $NH(C_{11}H_{11}ON_2)_2$, m. p. 104°. That the *iso*antipyrine- and antipyrine-reds have the formulæ assigned to them is very probable, since antipyrine-red may also be prepared by methylating rubazonic acid with methyl sulphate.

W. H. G.

1-Phenyl-5-methylpyrazole. RICHARD STOERMER (*Ber.*, 1907, **40**, 484—488).—The author has shown previously (Abstr., 1904, i, 181) that pyrazolones are reduced to pyrazoles by means of phosphorus tribromide. This method is now considered to be the most convenient one for the preparation of pyrazoles; for example, 1-phenyl-3-methylpyrazole may be obtained in theoretical yield from 1-phenyl-3-methylpyrazolone.

1-Phenyl-5-methylpyrazole, $C_{10}H_{10}N_2$, obtained by the reduction of 1-phenyl-5-methyl-3-pyrazolone with phosphorus tribromide, has b. p. 263·5°/762 mm., and is an oil with an odour recalling that of quinoline. When oxidised by permanganate, it forms 1-phenylpyrazole-5-carboxylic acid, m. p. 183°.

1-Phenyl-5-methylpyrazole *platinichloride* has m. p. 198—199°; the *aurichloride* has m. p. 124—125°; the *picrate* has m. p. 97—98°; the *methiodide* has m. p. 256—257°; the *ethiodide* has m. p. 208°.

The properties of 1-phenyl-5-methylpyrazole and its salts are contrasted with the results quoted by previous investigators.

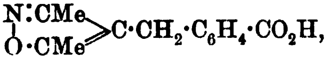
A. McK.

Acetylacetonebenzyl-*o*-carboxylic Acid and its Condensation Products. CARL BÜLOW and MAX DESENISS (*Ber.*, 1907, **40**, 187—192. Compare Bülow, Abstr., 1887, 144; Bülow and Koch, Abstr., 1904, i, 321).—*Acetylacetone-γ-benzyl-*o*-carboxylic acid*,

$$CH(COMe)_2\cdot CH_2\cdot C_6H_4\cdot CO_2H,$$

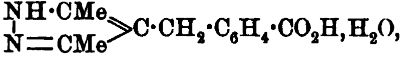
formed with development of heat by reduction of phthalylacetylacetone with zinc dust and acetic acid, crystallises in needles, sinters at 80°, m. p. 97°, is hydrolysed by boiling 20% potassium hydroxide, yielding benzylacetone-*o*-carboxylic acid, and when treated with ammonia in cooled absolute alcoholic solution forms *ammonium acetylacetonebenzyl-*o*-carboxylate* m. p. 140—150°, which loses ammonia when boiled with water.

The action of hydroxylamine hydrochloride and sodium acetate on acetylacetone-γ-benzyl-*o*-carboxylic acid in aqueous acetic acid solution leads to the formation of 4-o-*carboxybenzyl*-3 : 5-*dimethyl*iso-*oxazole*,



$\left.\begin{array}{l}\mathrm{N{:}CMe}\\ \mathrm{O\cdot CMe}\end{array}\right>\mathrm{C\cdot CH_2\cdot C_6H_4\cdot CO_2H}$, which separates in white crystals, m. p. 117—118°.

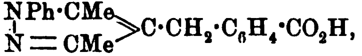
4-o-*Carboxybenzyl*-3 : 5-*dimethylpyrazole*,



$$\left.\begin{array}{l}\mathrm{NH\cdot CMe}\\ \mathrm{N{=}CMe}\end{array}\right>\mathrm{C\cdot CH_2\cdot C_6H_4\cdot CO_2H,H_2O},$$

prepared by boiling acetylacetonebenzyl-*o*-carboxylic acid with semicarbazide acetate in alcoholic or with hydrazine in glacial acetic acid solution, crystallises in needles, loses H_2O at 100—110°; m. p. 180°.

1-*Phenyl*-4-o-*carboxybenzyl*-3 : 5-*dimethylpyrazole*,



$$\left.\begin{array}{l}\mathrm{NPh\cdot CMe}\\ \mathrm{N{=}CMe}\end{array}\right>\mathrm{C\cdot CH_2\cdot C_6H_4\cdot CO_2H},$$

formed from phenylhydrazine and acetylacetonebenzyl-*o*-carboxylic acid, separates from alcohol in transparent crystals, m. p. 217—218°.

G. Y.

Preparation of 5 : 5-Dialkylbarbituric Acids. EMANUEL MERCK (D. R.-P. 174178).—When heated with concentrated acids (sulphuric, hydrochloric, benzenesulphonic, and naphthalenetrisulphonic acids) the dialkylmalonuramides yield 5 : 5-dialkylbarbituric acids. In this way diethylmalonuramide when heated with excess of concentrated sulphuric acid at 100—110° gives rise to 5 : 5-diethylbarbituric acid.

G. T. M.

Preparation of 2-Imino-4 : 6-dioxy-mono- and di-5-alkylpyrimidines. CHEMISCHE FABRIK AUF AKTIEN (vorm. E. Schering) (D. R.-P. 174940).—Although barbituric acid is not readily alkylated in alkaline or dilute alcoholic solutions, yet 2-imino-4 : 6-dioxypyrimidine (malonylguanidine) furnishes a good yield of alkyl derivatives. The interaction of 1 mol. of ethyl iodide in presence of potassium hydroxide gives rise to 2-imino-4 : 6-dioxy-5-ethylpyrimidine, whilst 2-imino-4 : 6-dioxy-5 : 5-diethylpyrimidine is formed when 2 mols. of alkyl iodide are employed. The yield of the latter product is, however, improved by alkylating in two stages.

G. T. M.

Indoleaminopropionic Acid and its Halogen Derivatives. The Tryptophan Reaction. CARL NEUBERG and NIKOLAUS POPOWSKY (*Biochem. Zeitsch.*, 1907, 2, 357—382. Compare Hopkins and Cole, Abstr., 1901, i, 310).—Pure tryptophan (indoleaminopropionic acid) may be obtained somewhat more readily from fibrin than from casein by Hopkins and Cole's method. From 600 grams of dried material 8 grams of tryptophan were obtained. It is a convenience to combine the preparation of tyrosine with that of tryptophan.

The reddish-violet coloration obtained by the addition of chlorine or bromine water to tryptophan attains a maximum when the amount of halogen is equivalent to 4 atoms per gram-mol. of tryptophan. When concentrated solutions are used, red, amorphous precipitates of monohalogen derivatives, $C_{11}H_{11}O_2N_2Br$ and $C_{11}H_{11}O_2N_2Cl$, are obtained. The compounds dissolve in amyl alcohol or ether, yielding reddish-violet solutions, and both decompose at about 280°. Excess of halogen converts the red compounds into yellow *perhaloids*, $C_{11}H_{11}O_2N_2Br_3$ and $C_{11}H_{11}O_2N_2Cl_3$, which contain two of the three halogen atoms only loosely combined.

The contradictory results obtained by previous authorities are due to their having worked with mixtures of the yellow and red compounds. No trace of sulphur is contained in the pure coloured substances. The nitrogen in tryptophan and its derivatives may be estimated by Kjeldahl's process. J. J. S.

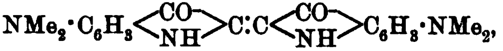
Preparation of Quinazoline from *o*-Nitrobenzaldehyde. J. D. RIEDEL (D. R.-P. 174941. Compare Abstr., 1904, i, 1060; 1905, i, 944).—The following operations afford a ready means of preparing quinazoline, a substance hitherto obtained only with some difficulty.

o-*Nitrobenzylidenediformamide*, $NO_2\cdot C_6H_4\cdot CH(NH\cdot CHO)_2$, produced by passing hydrogen chloride into a mixture of *o*-nitrobenzaldehyde (1 part) and formamide (2 parts) at 40—50°, is soluble in hot water and alcohol, but insoluble in ether; stellar aggregates of prisms, m. p. 177—178°. Quinazoline is obtained from this diformamide by reducing it with zinc dust and dilute acetic acid. G. T. M.

Di-*p*-dimethylaminoindigotin. MARTIN FREUND and ADOLF WIRSING (*Ber.*, 1907, 40, 204—206).—p-*Dimethylaminophenylglycinonitrile*, $NMe_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CN$, prepared by the action of hydrogen cyanide and formaldehyde on dimethyl-*p*-phenylenediamine in alcoholic solution at 100° under pressure, crystallises in colourless needles, m. p. 80—81°, and is hydrolysed by boiling aqueous potassium hydroxide forming p-*dimethylaminophenylglycine*,

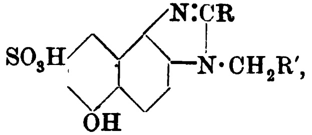
$$NMe_2\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO_2H,$$

m. p. 182—183°; the *potassium* salt, $C_{10}H_{13}O_2N_2K$, crystallises in glistening scales, commences to decompose at 280°, and is melted at 308°. When added to fused sodamide, the potassium salt forms *di*-p-*dimethylaminoindigotin*,



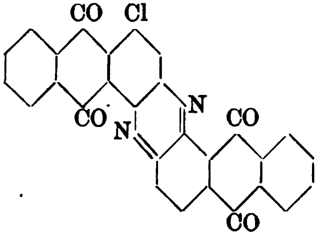
$$NMe_2\cdot C_6H_3{<}\begin{matrix}CO-\\NH\end{matrix}{>}C{:}C{<}\begin{matrix}CO-\\NH\end{matrix}{>}C_6H_3\cdot NMe_2,$$

which separates from water as a green, flocculent substance, does not melt or sublime when heated, forms bluish-green solutions in organic solvents, or blue solutions in dilute hydrochloric or concentrated sulphuric acid, dyes wool green in acetic acid solution or in presence of sodium hydrogen sulphite, and forms sparingly double *salts* with zinc, mercuric, and platinic chlorides. G. Y.

Preparation of 5-Hydroxynaphthaminobenzaldehydine-7-sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 175023. Compare Abstr., 1906, i, 989).—Hydroxynaphthaminobenzaldehydinesulphonic acids having the general formula 

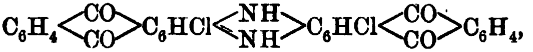
where R and R′ are dissimilar radicles, may be prepared by condensing 1 : 2-diamino-5-hydroxynaphthalene-7-sulphonic acid with the bisulphite compound of an aldehyde, whereby an intermediate product is obtained which can then be further condensed with a molecule of a second aldehyde.

The bisulphite compound of *m*-aminobenzaldehyde was condensed with the sulphonic acid and the intermediate product condensed with the bisulphite compound of benzaldehyde. The final product is a yellow, amorphous substance, sparingly soluble in alcohol or water, and having both acidic and weak basic properties. It combines with diazo-compounds and is readily diazotised, giving an insoluble diazo-derivative which is reddened by alkalis. G. T. M.



Indanthrene and Flavanthrene. III. The Halogen Derivatives of Indanthrene. Roland Scholl, Hans Berblinger, and Johannes Mansfield (*Ber.*, 1907, 40, 320—325. Compare Abstr., 1904, i, 110).—4-*Chloroanthraquinonazine*, prepared by the oxidation of 4-chloroindanthrene with nitric acid, D 1·285, on the water-bath, has a greenish-yellow colour somewhat darker than anthraquinonazine.

4 : 4′-*Dichloroindanthrene*,



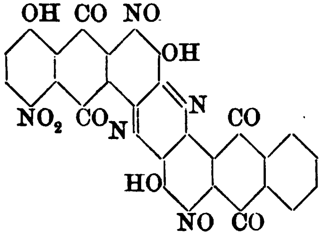
$$C_6H_4{<}\substack{CO\\CO}{>}C_6HCl{<}\substack{NH\\NH}{>}C_6HCl{<}\substack{CO\\CO}{>}C_6H_4,$$

is obtained as a blue powder when the monochloro-derivative is heated for three hours at 180° with hydrochloric acid.

4-*Bromoindanthrene*, $C_{28}H_{13}O_4N_2Br$, prepared by heating anthraquinonazine with hydrobromic acid, D 1·47, for two hours at 150° in in a closed tube, crystallises from quinoline in slender blue needles with a copper-red reflex. It is oxidised to 4-*bromoanthraquinonazine*, $C_{28}H_{11}O_4N_2Br$, by nitric acid, D 1·285. It is greenish-yellow and dissolves more easily in concentrated sulphuric acid than the parent azine. 4-4′-*Dibromoindanthrene*, $C_{28}H_{12}O_4N_2Br_2$, prepared similarly to the dichloro-derivative, is blue and has not been obtained quite pure. 4 : 4-*Dibromoanthraquinonazine* 3 : 4-*dibromide*, $C_{28}H_{10}O_4N_2Br_4$, is prepared by heating indanthrene with bromine in a sealed tube at 100° for six hours. The dark green base is converted into 3 : 4 : 4′-*tribromoindanthrene*, $C_{28}H_{11}O_4N_2Br_3$, by boiling quinoline, and crystallises in slender blue needles. W. R.

Indanthrene and Flavanthrene. IV. Action of Nitric Acid on Indanthrene. Roland Scholl and Johannes Mansfield (*Ber.*, 1907, 40, 326—329).—Boiling dilute nitric acid, D 1·24, oxidises indanthrene to anthraquinonazine, but when boiling acid is employed, a nitrodinitrosotrihydroxy- or tetranitrotetrahydroxyanthraquinonazine is obtained according to the conditions.

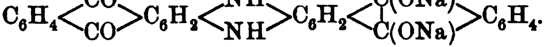
Nitrodinitrosotrihydroxyanthraquinonazine, $C_{28}H_9O_{11}N_5$, obtained by boiling 1 part of indanthrene with 12 to 15 parts of nitric acid, D 1·4, for twelve hours, is a yellow, crystalline powder when crystallised from concentrated nitric acid or nitrobenzene; it dissolves in sulphuric acid with a yellowish-red colour. The *sodium* salt is black. The compound is of the nature of a nitro- or nitroso-phenol, as it dissolves in aqueous sodium carbonate; no nitro- or nitroso-group is attached to an azine nitrogen atom, as boiling phenol is without action. The constitution provisionally assigned is as here given. On reduction with excess of dilute sodium hydrogen sulphide at 70—80°, *triaminotrihydroxyindanthrene*, $C_{28}H_{17}O_7N_5$, is obtained, and crystallises from nitrobenzene in violet-black needles; the *hydrochloride* is yellow, and the base is sparingly soluble in hot dilute sodium hydroxide.



Tetranitrotetrahydroxyanthraquinonazine, $C_{28}H_8O_{16}N_6$, is obtained by boiling indanthrene in a mixture of fuming nitric acid, D 1·5, and sulphuric acid, and yields, on reduction with sodium hydrogen sulphide, *tetra-aminotetrahydroxyindanthrene*, $C_{28}H_{18}O_8N_6$.

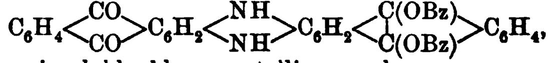
Nitrodinitrosotrihydroxyanthraquinonazine dyes cotton substantively a wine red, but the two amino-compounds are of no technical value as dyes for vegetable fibres. W. R.

Indanthrene and Flavanthrene. V. Reduction Products of Indanthrene. Roland Scholl, Wilhelm Steinkopf, and A. Kabacznik (*Ber.*, 1907, **40**, 390—394. Compare Abstr., 1904, i, 109, 110, and preceding abstracts).—The blue substance formed by reduction of indanthrene by means of sodium hydrogen sulphite in aqueous sodium hydroxide solution, and termed commercially "indanthrene S," is the *disodium* derivative of *N*-dihydro-1 : 2 : 1′ : 2′-anthraquinoneanthrahydroquinonazine (dihydroindanthrene),



$$C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{NH\\NH}>C_6H_2<\substack{C(ONa)\\C(ONa)}>C_6H_4.$$

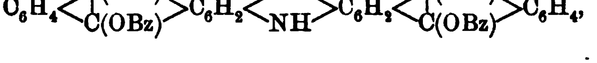
When treated with benzoyl chloride and sodium hydroxide it yields a *dibenzoyl* derivative,



$$C_6H_4<\substack{CO\\CO}>C_6H_2<\substack{NH\\NH}>C_6H_2<\substack{C(OBz)\\C(OBz)}>C_6H_4,$$

which is obtained as an insoluble, blue, crystalline powder.

The yellowish-brown substance formed by reduction of indanthrene by means of sodium hydrogen sulphite and zinc dust is the *tetrasodium* derivative of tetrahydroindanthrene; it cannot be isolated in consequence of the ease with which it is oxidised, yielding finally indanthrene. The *tetrabenzoyl* derivative,



$$C_6H_4<\substack{C(OBz)\\C(OBz)}>C_6H_2<\substack{NH\\NH}>C_6H_2<\substack{C(OBz)\\C(OBz)}>C_6H_4,$$

formed by the action of benzoyl chloride and sodium hydroxide on the reduction product, is obtained as a brownish-yellow, microcrystalline powder, m. p. above 300°, which dissolves in chloroform, benzene, ψ-cumene, or ethyl benzoate, forming a solution with green fluorescence.

G. Y.

Indanthrene and Flavanthrene. VI. Action of Quinoline and Acyl Chlorides on Indanthrene. ROLAND SCHOLL and HANS BERBLINGER (*Ber.*, 1907, **40**, 395—400. Compare preceding abstracts).—The action of benzoyl chloride on indanthrene in boiling quinoline solution leads to the formation of the tetrabenzoyl derivative of tetrahydroindanthrene, which, when heated, yields a sublimate of benzoic acid and dissolves in alcoholic potassium hydroxide, forming a blue solution depositing indanthrene on dilution and exposure to air. It is oxidised by concentrated nitric acid, yielding the *nitrate* of tetrabenzoylanthrahydroquinonazine, which forms an indigo-blue solution and is hydrolysed on heating with the acid, forming a soluble, brown anthraquinonazine. When boiled with quinoline, the tetrabenzoyltetrahydroindanthrene is converted slowly into anthranonazine.

*Tetra-acetyl-*N*-dihydroanthrahydroquinonazine* is formed slowly by boiling indanthrene with acetyl chloride and quinoline in glacial acetic acid solution; it crystallises in microscopic, brownish-yellow needles, dissolves in organic solvents, forming reddish-yellow solutions with green fluorescence, and is converted into dihydroindanthrene by the action of alcoholic potassium hydroxide. On prolonged boiling with quinoline, it yields anthranonazine, which is formed more rapidly by the action of acetyl chloride on indanthrene in boiling quinoline solution in the absence of acetic acid.

The formation of *O*-acyl derivatives of a reduced indanthrene instead of substitution of the imine hydrogen atoms must result from increased stability of these when in proximity to carbonyl groups (compare Abstr., 1904, i, 109), as is the case with the hydroxyl-hydrogen of the aldol of diacetyl (von Pechmann, Abstr., 1895, i, 647). The reducing action of acid anhydrides or acyl chlorides on quinones and similar substances has been observed in other cases; thus, methylene-blue is converted into the acetyl derivative of the leuco-compound when heated with acetic anhydride and sodium acetate, a reaction which takes place also with thiazine and oxazine dyes (compare Japp and Graham, Trans., 1881, **39**, 174).

G. Y.

Action of Hydrogen Sulphide on Rosaniline and Phenylated Rosanilines. RUDOLF LAMBRECHT (*Ber.*, 1907, **40**, 247—255. Compare Abstr., 1905, i, 243).—The action of hydrogen sulphide on rosanilines is explicable on the assumption of the intermediate formation of a hydrosulphide, $\text{:C:C}_6\text{H}_4\text{:NH}_2\cdot\text{SH}$; attempts to isolate such a compound, however, lead to the formation of a quinonoid oxidation product of unknown constitution.

In acid or neutral alcoholic solution, hydrogen sulphide reduces *p*-rosaniline to the leucaniline; excess of ammonium hydrosulphide produces *triaminotriphenylcarbothiol*, $C_{19}H_{19}N_3S$. The carbothiol forms colourless solutions in mineral acids, but loses hydrogen sulphide in alcohol-acetic acid solution. It dissolves in alcohol to an intensely magenta coloured solution, by the evaporation of which a quinonoid substance is obtained; a similar greenish-red glistening substance is formed when the carbothiol is heated at 140°.

Triaminotritolylcarbothiol, $C_{22}H_{25}N_3S$, obtained from new magenta in a similar manner to the preceding compound, yields the carbinol base by treatment with alkalis, and in alcoholic solution is converted into quinonoid products.

p-Rosaniline-blue (Kalle & Co.), treated with hydrogen sulphide in alcoholic solution, yields triphenyl-*p*-leucaniline, m. p. 182°, whereas excess of ammonium hydrosulphide produces the carbinol base,

$$C(C_6H_4{\cdot}NHPh)_3{\cdot}OH.$$

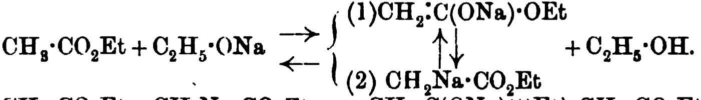
Diphenylamine-blue is an impure triphenyl-*p*-rosaniline, since by treatment with alcoholic hydrogen sulphide it yields impure triphenyl-*p*-leucaniline, m. p. 178°.

Rosaniline-blue is reduced to the *leuco*-compound

$$CH(C_6H_4{\cdot}NHPh)_2{\cdot}C_7H_6{\cdot}NH_2,\ \text{m. p. } 116°,$$

by alcoholic hydrogen sulphide, and yields the carbinol base by treatment with excess of ammonium hydrosulphide. C. S.

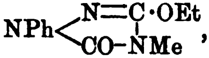
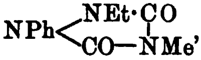
Urazoles. VIII. Sale of Tautomeric Compounds. SALOMON F. ACREE (*Amer. Chem. J.*, 1907, 37, 71—85).—This paper deals with the behaviour of the metallic salts of tautomeric acids. The relations between the concentration of solutions of such salts and the equilibrium constants are discussed. It is considered that all syntheses analogous to the ethyl acetoacetate synthesis depend on the reactions of tautomeric salts. Thus, in the formation of ethyl acetoacetate from ethyl acetate and sodium ethoxide, a sodium salt of ethyl acetate is formed, which exists in two tautomeric forms. The sodium salt (2) reacts vigorously with the ethyl acetate present, and ethyl acetoacetate is formed in accordance with the following scheme:



$$CH_3{\cdot}CO_2Et + C_2H_5{\cdot}ONa \rightleftarrows \left\{\begin{array}{c}(1)CH_2{:}C(ONa){\cdot}OEt \\ \uparrow\downarrow \\ (2)\ CH_2Na{\cdot}CO_2Et\end{array}\right. + C_2H_5{\cdot}OH.$$

$$CH_3{\cdot}CO_2Et + CH_2Na{\cdot}CO_2Et \longrightarrow CH_3{\cdot}C(ONa)(OEt){\cdot}CH_2{\cdot}CO_2Et$$
$$\longrightarrow CH_3{\cdot}C(ONa){:}CH{\cdot}CO_2Et + C_2H_5{\cdot}OH.$$

It is well known that when the silver salts of certain amides are treated with alkyl halides at the ordinary temperature, oxygen ethers are formed principally, whilst the potassium salts at higher temperatures yield chiefly the nitrogen compounds. The theories which have been advanced by Comstock, Wheeler, Nef, and Michael to account for such reactions are discussed and shown to be inadequate. In place of these the following hypothesis is brought forward. "A salt of a tautomeric compound reacts with an alkyl halide or other reagent and forms two compounds, because the tautomeric salt is really a mixture of two tautomeric salts in equilibrium, each of which reacts with the alkyl halide in independent side reactions. This reaction may, in certain cases, be complicated by the simultaneous rearrangement of one of the reaction products into the other or into some other product."

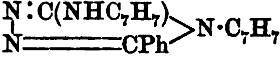
This theory is supported by the results of experiments which have been carried out with a view of ascertaining the conditions of equilibrium which exist in solutions of salts of 1-phenyl-4-methylurazole. When a salt of this urazole is heated with ethyl iodide in solution in dilute alcohol, ether, or benzene, a mixture of 3-ethoxy-1-phenyl-4-methylurazole,  $NPh<\begin{matrix}N{=}C\cdot OEt\\ CO{-}NMe\end{matrix}$, and 1-phenyl-4-methyl-2-ethylurazole,  $NPh<\begin{matrix}NEt\cdot CO\\ CO{-}NMe\end{matrix}$, is produced. The proportions in which these two compounds are formed varies with the salt employed. Thus, in dilute alcohol (40%), 90% of the *N*-ethyl and 10% of the *O*-ethyl derivatives are produced. In the same solvent, the barium salt gives 93·5% of the former and 6·5% of the latter, whilst the sodium salt yields 58·7% of the *O*-compound and 41·3% of the *N*-compound. The silver salt in ether gives 35% of the *N*-ethyl and 65% of the *O*-ethyl derivatives. The determination of these ratios at 22°, 60°, and 90° shows that each is nearly constant, or the two side reactions have approximately the same temperature coefficient. Neither of the two derivatives undergoes rearrangement into the other under any of the conditions studied. The proportions in which the two compounds are produced vary not only with the salt and the solvent employed, but also with the particular alkyl halide used; thus, whilst in dilute alcohol (40%) at 60°, the potassium salt reacts with ethyl iodide in one hour to the extent of 30·35%, and 90% of the product consists of the *N*-ethyl derivative; the same salt reacts with ethyl bromide under the same conditions to the extent of 22·5%, and the *N*-ethyl derivative forms 87·7% of the product. E. G.

Triazoles. MAX BUSCH (*J. pr. Chem.*, 1906, [ii], **74**, 533—549. Compare Abstr., 1906, i, 115).—An attempt to prepare acyl*endo*iminotriazoles by the action of formic acid on benzoylaminodiarylguanidines failed, as the action leads to the formation of the colourless, feebly basic 5-aminotriazoles formed previously by heating the acylaminoguanidines (Busch and Bauer, Abstr., 1900, i, 414).

Triazoles from benzoylaminodiarylguanidines.—[With HERM. BRANDT.]—The action of carbodiphenylimide on benzhydrazide in benzene solution at 50° leads to the formation of benzoylaminodiphenylguanidine and 5-anilino-1 : 2-diphenyl-1 : 2 : 3-triazole, which are separated by conversion of the slightly acid guanidine into its soluble *sodium* salt. When oxidised with alcoholic ferric chloride, benzoylaminodiphenylguanidine yields a blue *product* which is probably the *azo*-compound, $NHPh\cdot C(NPh)\cdot N{:}NBz$.

The anilinotriazole, which is the chief product of the action of carbodiphenylimide on benzhydrazide in boiling benzene solution, is formed also by heating benzoylaminodiphenylguanidine with formic acid in a sealed tube at 170°; it yields only traces of aniline and benzoic acid when heated with concentrated hydrochloric acid under pressure at 200°.

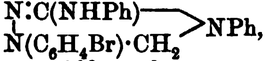
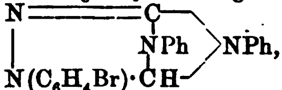
The following tolyl compounds are prepared in the same manner.

Benzoylaminodi-o-tolylguanidine, $C_7H_7\cdot NH\cdot C(N\cdot C_7H_7)\cdot NH\cdot NHBz$, crystallises from alcohol in nodular aggregates, m. p. 151°, intumescing, and, when heated above its melting point, forms water and 5-o-*toluidino*-2-*phenyl*-1-o-*tolyltriazole*,  $\left.\begin{array}{l}N{:}C(NHC_7H_7)\\ \mid\\ N{=\!=\!=}CPh\end{array}\right>N\cdot C_7H_7$, which is obtained as a white, crystalline powder, m. p. 142°.

Benzoylaminodi-p-*tolylguanidine*, $C_{22}H_{22}ON_4$, forms yellow, transparent prisms, m. p. 190°, intumescing.

5-p-*Toluidino*-2-*phenyl*-1-p-*tolyltriazole*, $C_{22}H_{20}N_4$, crystallises in glistening spears, m. p. 196°.

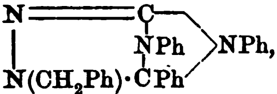
The action of carbodiphenylimide on semicarbazide leads to the formation of ammonia, carbon dioxide, hydrazodicarboxylamide, triphenylguanazole, and triphenylguanidine.

endo*Iminotriazoles*.—[With Herm. Brandt.]—p-*Bromoanilinodiphenylguanidine*, $NHPh\cdot C(NPh)\cdot NH\cdot NH\cdot C_6H_4Br$, prepared from *p*-bromophenylhydrazine and carbodiphenylimide, is obtained as a white, crystalline powder, m. p. 141°. When boiled with formaldehyde in alcoholic solution, it forms 3-*anilino*-4-*phenyl*-1-p-*bromophenyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,  $\left.\begin{array}{l}N{:}C(NHPh)\\ \mid\\ N(C_6H_4Br)\cdot CH_2\end{array}\right>NPh$, which crystallises in sheaves of needles, m. p. 119°, and on successive treatment with sodium nitrite and nitric acid in glacial acetic acid solution yields the sparingly soluble *nitrate* of 4-phenyl-1-*p*-bromophenyl-3 : 5-*endo*-anilo-4 : 5-dihydro-1 : 2 : 4-triazole, $C_{20}H_{15}N_4Br,HNO_3$, crystallising in slender needles; the free *base* (*bromonitron*),  crystallises in stout, glistening needles, m. p. 223° (decomp.); the nitrate is slightly more, the *hydrochloride* and *sulphate* less, soluble than the corresponding nitron salts.

a-*Naphthylaminodiphenylguanidine*, $C_{23}H_{20}N_4$, prepared from a-naphthylhydrazine and carbodiphenylimide, crystallises from benzene in colourless leaflets containing benzene of crystallisation, m. p. 143°, and is oxidised by mercuric oxide in alcoholic solution, yielding the *azo*-compound, $NHPh\cdot C(NPh)\cdot N{:}N\cdot C_{10}H_7$, which forms deep bluish-violet, glistening needles, m. p. 148°. When heated with formic acid at 180°, the aminoguanidine yields 4-*phenyl*-1-*a-naphthyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, which crystallises in yellow leaflets, m. p. 212°; the *nitrate*, $C_{24}H_{19}O_3N_5$, forms a microcrystalline powder, m. p. 219°, and is much more easily soluble than nitron nitrate.

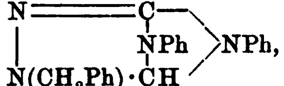
β-*Naphthylaminodiphenylguanidine* crystallises in needles, m. p. 152°; the *azo*-derivative forms dark violet, glistening prisms, m. p. 172°, and dissolves in alcohol, forming a red solution which gradually becomes colourless in consequence of the formation of chloronaphthyldiphenylaminoguanidine (compare Abstr., 1906, i, 465). *Phenyl-β-naphthyl*endo*anilodihydrotriazole* crystallises in light yellow leaflets, m. p. 205° (decomp.); the *nitrate* crystallises in slender needles, m. p. 238°, and is only slightly less insoluble than nitron nitrate; the *hydrochloride* and *sulphate* are also only sparingly soluble.

4 : 5-*Diphenyl*-1-*benzyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



formed by the action of benzoyl chloride on benzylaminodiphenylguanidine, crystallises from alcohol in slender, yellow needles, m. p. 186°; the *nitrate*, $C_{27}H_{22}N_4,HNO_3$, crystallises in needles, m. p. 239°, and is comparatively soluble in water.

4-Phenyl-1-*benzyl*-3 : 5-endo*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*,



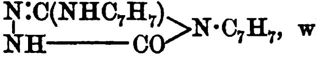
is obtained by heating benzylaminodiphenylguanidine with formaldehyde in alcoholic solution, and oxidising the resulting dihydrotriazole with sodium nitrite in glacial acetic acid; it forms yellow crystals, m. p. 129°; the *nitrate* is only sparingly soluble in water.

Action of Carbodi-imides on 4-*Phenylsemicarbazide*.—[With Gustav Blume.]—The action of carbodiphenylimide on 4-phenylsemicarbazide in benzene solution leads to the formation of 1-*diphenylguanyl*-4-*phenylsemicarbazide* [*phenylcarbamyldiphenylguanidine*],

$$NHPh\cdot C(NPh)\cdot NH\cdot NH\cdot CO\cdot NHPh,$$

which crystallises in slender, white needles, m. p. 171° (decomp.), and is soluble in dilute mineral acids or acetic acid; the product of its decomposition when heated is 3-anilino-4-phenyl-5-triazolone (Abstr., 1902, i, 574).

Di-o-*tolylguanyl*-4-*phenylsemicarbazide*, $C_{22}H_{23}ON_5$, formed from di-*o*-tolylcarbimide and 4-phenylsemicarbazide, crystallises in white needles, m. p. 164°, decomposing with formation of aniline and 3-o-*toluidino*-4-o-*tolyl*-5-*triazolone*,



$$\begin{matrix} N{:}C(NHC_7H_7) \\ | \qquad\qquad\quad | \\ NH\text{———}CO \end{matrix}\!\!>\!N\cdot C_7H_7,$$

which crystallises from alcohol in colourless prisms, m. p. 183°, and has feeble, basic, and acid properties.

G. Y.

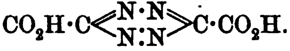
Behaviour of the Group N·C·N towards Acylating Agents. II. Gustav Heller (*Ber.*, 1907, 40, 114—119. Compare Abstr., 1904, i, 942).—The author has studied the behaviour on benzoylation of tetrazole as a type of a cyclic compound containing the group N·C·N and containing more than two nitrogen atoms.

When a mixture of equal amounts of ethyl alcohol and concentrated sulphuric acid is slowly added to a mixture of ethyl formazylcarboxylate, ethyl alcohol, and amyl nitrite, *ethyl diphenyltetrazoliumcarboxylate ethosulphate*, $C_{18}H_{20}O_6N_4S$, separates as glistening needles, m. p. 214—215° (decomp.). When a mixture of dilute nitric acid and potassium permanganate is added to its aqueous solution heated to 75°, it is oxidised to tetrazole.

When tetrazole in pyridine solution is acted on by benzoyl chloride, it forms, in addition to a dark yellow, non-crystalline substance, dibenzoylcarbamide, m. p. 210°. Tetrazole alone, however, is acted on by benzoyl chloride, when heated at 100°, with evolution of nitrogen and formation of *dibenzoylhydrazine*, which separates from alcohol in fine needles, m. p. 237°. Dibenzoylhydrazine is also formed by the interaction of benzoyl chloride and 1 : 2 : 4-triazole.

A. McK.

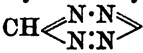
1:2:4:5-Tetrazine. THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, **40**, 84—88. Compare Curtius, Abstr., 1889, 369; Hantzsch and Lehmann, Abstr., 1901, i, 132; Curtius, Darapsky, and Müller, Abstr., 1906, i, 939; this vol., i, 21).—The authors had previously shown that the acid formerly described by Curtius, and by Hantzsch and Lehmann, as bisazoxyacetic acid is in reality 1:2:4:5-tetrazine-3:6-carboxylic acid,



$$CO_2H\cdot C\lessdot\begin{matrix}N\cdot N\\ N:N\end{matrix}\gtrdot C\cdot CO_2H.$$

It is now shown that when this acid is heated, the product obtained is not bisazoxymethane as described by Hantzsch and Lehmann, but is rfee from oxygen and is 1:2:4:5-tetrazine.

When 1:2:4:5-tetrazine-3:6-carboxylic acid is heated with dry sand at about 160°, a purple vapour is evolved which condenses as red crystals. By heating the latter with barium oxide, 1:2:4:5-*tetrazine*,



$CH\lessdot\begin{matrix}N\cdot N\\ N:N\end{matrix}\gtrdot CH$, is obtained as glistening, purple pyramids, m. p. 99°. (The bisazoxymethane of Hantzsch and Lehmann is described as having m. p. 75°.) The absorption spectra of its vapour and of its solutions were examined. Its solutions in water, alcohol, and in other solvents are bright red, and may be boiled for some time without undergoing decomposition.

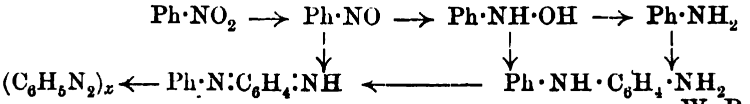
When 1:2:4:5-tetrazine is dissolved in concentrated hydrochloric acid, the solution is at first deep red, but nitrogen is soon evolved and the solution becomes colourless.

When hydrogen sulphide is passed into a solution of 1:2:4:5-tetrazine in water or in benzene, the dark red colour gradually disappears and sulphur is deposited; the red colour is restored when dilute acetic acid and sodium nitrite are added. When the tetrazine is reduced it forms a dihydro-derivative, which is readily reoxidised to the tetrazine.

A. McK.

Emeraldine. W. NOVER (*Ber.*, 1907, **40**, 288—297).—A new green electrolytic reduction product of nitrobenzene is formed in small quantities at a nickel gauze cathode when the cathode electrolyte is either a 50% solution of sodium hydrogen sulphate or a hydrofluosilicic acid solution of D 1·3. Its constitution was determined by preparing it either by oxidising *p*-aminodiphenylamine with ferric chloride or nitrosobenzene, or by shaking β-phenylhydroxylamine with sodium hydrogen sulphate. It is also prepared by the polymerisation of phenylquininedi-imide with acids (compare Caro, *Chem. Zeit.*, 1896, **21**, 840). By treatment of the green salt so obtained with sodium hydroxide and crystallisation from a mixture of light petroleum and xylene, emeraldine, $(C_6H_5N_2)_x$, is obtained as a blue, amorphous substance giving a carmine-red coloration with concentrated sulphuric acid.

The formation of emeraldine in the cell is supposed to be due to the following changes:



W. R.

Preparation of *o*-Hydroxyazo-derivatives. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 175827).—Diazotised *o*-aminophenol and its derivatives, containing neither nitro, nor sulphonic groups, do not readily couple with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid in the presence of aqueous alkali hydroxides. When, however, the coupling is effected in the presence of milk of lime the reaction proceeds smoothly, and a good yield of the pure product is obtained. The disulphonic acid is employed in the form of its disodium salt, and the calcium hydroxide emulsion and the diazo-solution are added successively. The mixture is left for some hours in order that the condensation may be completed, and the azo-derivative is freed from the calcium hydroxide by means of acid and then salted out in the usual way. The patent contains a table giving the properties of the azo-dyes prepared by this method from seventeen derivatives of *o*-aminophenol.

G. T. M.

Hyposulphites. IV. Action of Sodium Hyposulphite on Diazo-Salts. Eugène Grandmougin (*Ber.*, 1907, **40**, 422—423. Compare Abstr., 1906, i, 716, 967; this vol., i, 166).—When a solution of diazobenzene sulphate or chloride is added to a cold well-stirred suspension of sodium hyposulphite in water, a mixture of diazobenzeneimide and benzenesulphonphenylhydrazide (m. p. 164·5°, not 148—150°; compare W. Königs, Abstr., 1877, 219) is precipitated; sodium phenylhydrazine-*β*-sulphonate, the chief product of the reaction, is obtained from the mother liquor. Phenol and a small quantity of phenyl disulphide are formed when warm hyposulphite solution is used.

W. R.

[The Orientation of Sulphonated Chlorotoluene-azo-*β*-naphthols and their Lake-forming Properties.] Badische Anilin- & Soda-Fabrik (D.R.-P. 175378 and 175396).—6-Chloro-*p*-toluidine-3-sulphonic acid furnishes a sparingly soluble diazo-derivative which, when coupled with *β*-naphthol, yields an azo-dye forming very sparingly soluble calcium, barium, aluminium, and lead salts. These salts have a brilliant scarlet hue, which is affected neither by acids nor alkalis, and is very fast to light. The following isomerides: 5-chloro-*p*-toluidine-3-sulphonic, 4-chloro-*o*-toluidine-5-sulphonic, and 5-chloro-*o*-toluidine-3-sulphonic acids give coloured salts, which, on account of their great solubility in water and their sensitiveness to scouring agents, cannot be employed as lakes.

The following bases: 4-chloro-*m*-nitroaniline, 6-nitro-4-*m*-xylidine and 2 : 5-dichloro-*p*-toluidine, when diazotised and combined with *β*-naphthol-3 : 6-disulphonic acid, yield azo-dyes giving insoluble dark red barium salts suitable for lakes. This property is found to be generally true of all derivatives of aniline which contain two substituent groups or atoms in positions adjacent to one another. The patent contains a table of bases which have been examined from this standpoint.

G. T. M.

Coloured Hydrazinesulphonic Acids. Julius Tröger and Georg Puttkammer (*Ber.*, 1907, **40**, 206—212. Compare Abstr., 1904, i, 118; 1906, i, 120, 993, 994; Farbenfabriken vorm. F. Bayer

& Co., D.R.-P. 163447).—The red azobenzene-*p*-hydrazinesulphonic acid, $N_2Ph\cdot C_6H_4\cdot NH\cdot NH\cdot SO_3H$, prepared previously by passing a current of sulphur dioxide through a cooled solution of diazobenzene sulphate, has now been synthesised (*a*) by the action of diazotised *p*-aminoazobenzene on potassium sulphite in cooled aqueous potassium carbonate solution and reduction of the resulting stable potassium azobenzenediazosulphonate, $N_2Ph\cdot C_6H_4\cdot N_2\cdot SO_3K$, by means of ammonium sulphide, and (*b*) by passing a current of sulphur dioxide into an aqueous solution of diazotised *p*-aminoazobenzene.

2 : 3′-Dimethylazobenzene-4-hydrazinesulphonic acid has been prepared in the same manner from 4-amino-2 : 3′-dimethylazobenzene by diazotisation, conversion into potassium 2 : 3′-dimethylazobenzene-4-diazosulphonate, and reduction of this with ammonium sulphide. The resulting hydrazinesulphonic acid forms a p-*toluidine* salt, m. p. 154°, which is identical with that obtained from the product of the action of sulphur dioxide on diazotised *m*-toluidine.

Potassium 2 : 3′-*dimethylazobenzene*-4′-*diazosulphonate*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot N_2\cdot SO_3K,$$

prepared by the action of potassium sulphite on diazotised 4′-amino-2 : 3-dimethylazobenzene, is obtained as an orange-red precipitate, and when reduced with aqueous ammonium sulphide yields the reddish-brown 2 : 3′-*dimethylazobenzene*-4′-*hydrazinesulphonic acid*,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot NH\cdot NH\cdot SO_3H.$$

This forms yellow *alkali* and *ammonium* salts, reduces ammoniacal silver solution, and when heated with aromatic aldehydes in sulphuric acid and alcohol gives a bluish-violet coloration.

The coloured hydrazinesulphonic acids condense with ketones in alcoholic-sulphuric or glacial acetic acid solution, forming coloured *sulphates* from which ammonia liberates the crystalline *hydrazones*.

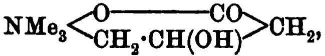
G. Y.

[An Azopyrazolone Derivative.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 175290).—*m*-Xylidine-*o*-sulphonic acid, when diazotised and coupled with phenylpyrazolonesulphocarboxylic acid, yields an azosulphocarboxylic acid which surpasses tartrazine in its tinctorial properties and in fastness to light. The new acid is precipitated from alkaline solutions by mineral acids and sodium chloride. G. T. M.

Extractives of Muscle. VI. Identity of Ignotine and Carnosine. WLADIMIR GULEWITSCH (*Zeitsch. physiol. Chem.*, 1906, **50**, 204—208).—Kutscher's ignotine (*Zeitsch. Nahr. Genussm.*, 1905, **10**, 528) is identical with carnosine (Abstr., 1900, i, 516); both melt and decompose at 241—245°. J. J. S.

Extractives of Muscle. VII. Compounds of Carnitine. R. KRIMBERG (*Zeitsch. physiol. Chem.*, 1907, **50**, 361—373. Compare Abstr., 1905, i, 726).—Carnitine yields two double salts with mercuric chloride. The one, $C_7H_{15}O_3N,2HgCl_2$, m. p. 196—197°, is formed when alcoholic solutions of the base or its carbonate and of mercuric chloride are mixed; it crystallises well and is sparingly soluble in water. The other, $C_7H_{15}O_3N,HCl,6HgCl_2$, is obtained from solutions containing an excess of hydrochloric acid, usually as an oil which slowly crystallises; it is more readily soluble than the other mercurichloride, from which it can be separated by fractional crystallisation. The compound with 2 mols. of mercuric chloride can be made use of for the isolation of carnitine.

Carnitine phosphotungstate crystallises in fan-shaped aggregates of needles. The *hydrochloride* is very hygroscopic and is lævorotatory. The *aurichloride*, $C_7H_{16}O_3N,AuCl_4$, crystallises in pale-yellow needles and orange-coloured needles and prisms, m. p. 150. The *nitrate* is also very hygroscopic. The formula,



$$NMe_3\left\langle\begin{matrix}O\text{———————}CO\\CH_2\cdot CH(OH)\end{matrix}\right\rangle CH_2,$$

is suggested for the base. J. J. S.

Caseinokyrine. III. Max Siegfried (*Zeitsch. physiol. Chem.*, 1906, **50**, 163—173. Compare Abstr., 1905, i, 104).—Further examination has shown that the specimens of caseinokyrine previously obtained were pure. The fact that Skraup and Witt's preparations (Abstr., 1906, i, 916) were not pure is due to the fact that they did not follow the details of the author's method of purification.

The carbamino-reaction (Abstr., 1905, ii, 332; 1906, i, 144) has been employed in the case of caseinokyrine and the ratio CO_2/N found to be 1/2·25. For the products of hydrolysis the ratio is 1/1·5.

J. J. S.

Light Absorption of Hæmoglobin. Hans Aron and Franz Müller (*Zeitsch. physiol. Chem.*, 1907, **50**, 443—444).—Polemical against R. von Zeynek (this vol., i, 167). W. D. H.

The Gradual Hydrolysis of the Oxyhæmoglobin of the Horse. Hugo Kirbach (*Zeitsch. physiol. Chem.*, 1906, **50**, 129—162. Compare Siegfried, Abstr., 1905, i, 104).—A basic complex *globinokyrine*, analogous to Siegfried's caseinokyrine, has been isolated from the products obtained by the hydrolysis of pure recrystallised horse's oxyhæmoglobin with 12% sulphuric acid at 37—40°. It may be precipitated by means of phosphotungstic acid and purified by conversion into the sulphate; the yield of crude sulphate varying from 50 to 60 grams per 10 litres of blood. Neither phosphotungstate nor sulphate could be obtained in a crystalline form. The base and its sulphate dissolve readily in water and the base is insoluble in ether and practically insoluble in alcohol; it gives the biuret, but not Millon's, reaction. The sulphate is optically inactive and gives the Congo-reaction. The mean analytical data obtained from several pure specimens are C, 34·26; H, 5·89; N, 15·08; S, 10·95, and O, 33·73%. When hydrolysed with 33·3% sulphuric acid the sulphate yields histidine, arginine, lysine, and glutamic acid. Of the total nitrogen in the hydrolytic products, the proportions due to the bases and to the amino-acids have been determined and also the proportions due to each product of hydrolysis. The results agree with the view that the nitrogen in the kyrine is distributed between 2 mols. of histidine, 1 of arginine, 2 of lysine, and 4 of glutamic acid. J. J. S.

Preparation and Analysis of Nucleic Acids. XII. Nucleic Acid from the Spermatozoa of the Shad. (Alosa). PHŒBUS A. LEVENE and JOHN A. MANDEL (*Zeitsch. physiol. Chem.*, 1906, **50**, 1–10. Compare Abstr., 1906, i, 125, 468; this vol., i, 168).—The nucleic acid from the spermatozoa of the shad contains C, 36·27; H, 5·00; N, 15·96, and P, 8·11%. In the estimation of purine bases, much smaller yields of guanine are obtained when the copper nucleate is hydrolysed instead of the free acid. The purine bases isolated were adenine, guanine, thymine; and, in addition, cytosine and lævulic acid were obtained. J. J. S.

Nucleic Acids from the Thymus. IVAR BANG (*Zeitsch. physiol. Chem.*, 1907, **50**, 442).—Polemical against Steudel (Abstr., 1904, i, 837; 1905, i, 398; 1906, i, 125; this vol., i, 168). W. D. H.

Peptones from Albumins. II. Peptones Derived from Blood Albumin and Precipitated by Potassium Mercury Iodide. HENRY S. RAPER (*Beitr. Chem. Physiol. Path.*, 1907, **9**, 168–182. Compare Stookey, Abstr., 1906, i, 327).—The potassium mercury iodide peptone precipitate, obtained after blood albumin had been fermented with pepsin and sulphuric acid for six weeks, was extracted with water in which some two-thirds dissolved *B*, the residue *A* dissolved completely in 5% ammonium carbonate solution. A portion of *B* dissolved in alcohol, *Ba*, but a considerable amount was insoluble, *Bβ*. The phenylcarbimide derivative from fraction *A* was prepared and resolved into three separate fractions by conversion of the carbamide into its sodium salt and precipitating this with carbon dioxide and extracting with hot alcohol. The fraction *Aa* was insoluble in alcohol, *Ab* separated out at 0°, and *Ac* was obtained on removal of the alcohol. The m.p.'s are respectively 203—205°, 178—180°, and 169—170°. From *p*-bromophenylcarbimide a bromo-derivative corresponding with fraction *Ab* was prepared. The percentage composition agrees with the formula $C_{64}H_{89}O_{18}N_{16}Br_8$, m. p. 184—185°. The bromo-derivative corresponding with the fraction *Ac* has the composition $C_{34}H_{46}O_9N_8Br_2$, m. p. 173—175°.

The phenylcarbimide derivative *Ac*, when hydrolysed with concentrated sulphuric acid, yields lysine, proline, leucine, tyrosine, aniline, ammonia, glutamic acid, a base, m. p. 231—233°, and a product, m. p. 110—112°, and soluble in ether.

From fraction *B* two phenylcarbimide derivatives were obtained. The one *Ba* is soluble in 10% alcohol and has m. p. 167—169°. None of the compounds could be obtained in a crystalline form.

J. J. S.

Protamines and Histones. ALBRECHT KOSSEL and H. PRINGLE (*Zeitsch. physiol. Chem.*, 1906, **49**, 301—321. Compare Abstr., 1905, ii, 467).—The simplest protamines are those of the salmine group (salmine, clupeine, scombrine); 8/9ths of the nitrogen present is in the form of arginine, the remaining 1/9th as monoamino-acids; alanine, serine, aminovaleric acid, and proline. Two or more of these mono-acids may be present. As arginine contains 4 atoms of nitrogen, it follows that 1 molecule of monoamino-acid is present to every 2 molecules of arginine, and such protamines are therefore diarginyl compounds. Reasons are given for believing that the linkage is symmetrical, thus: *aab′*, *aab″*, *aab‴*, where *a* is arginyl and *b′*, *b″*, *b‴* monoamino-groups. The protones obtained as the first cleavage products from these protamines also contain 8/9ths of their nitrogen in the form of arginine. Diarginylalanine will have the molecular weight, 401, diarginylserine, 417, diarginylproline, 427, and diarginylaminovaleric acid, 429. The boiling point and freezing point methods of determination gave the molecular weight of the protones as from 419 to 423. It therefore appears that the protones are mixtures of the diarginyl compounds just enumerated. By the action of nitrous acids on this mixture, ornithine is split off, from which it is argued that the symmetric arrangement is probably *b a a* rather than *a a b* or *a b a*. It is only by considering such simple cases that the study of more complex proteids becomes possible. In histones, arginine is again the most abundant cleavage product (24% to 26% of the total nitrogen), and lysine comes next (7% to 8%). From various histones the substance called histopeptone was prepared by peptic digestion; this yields the same proportion of arginine, but it appears to be a chemical unit, not a mixture as the protones are. The method of obtaining this substance by the silver-baryta method is given. Globin is not regarded as a histone. W. D. H.

Histopeptone. T. KRASNOSSELSKY (*Zeitsch. physiol. Chem*, 1906, **49**, 322—323).—Attempts to obtain histopeptone (see preceding abstract) from various vegetable proteids failed. It was, however, obtained by Kossel's method from various animal organs, namely, from the testes of the cod and the spleen. The percentage of nitrogen in the former preparation was 19·5, in the latter 19·7. Kossel found it to be 19·9 in the histopeptone prepared from thymus. Histopeptone was also obtained from liver, lymph glands, intestinal mucous membrane, and red marrow. The most abundant yield was from the spleen, the least from the liver. W. D. H.

Action of Ultra-violet Light on Invertase. A. JODLBAUER and HERMANN VON TAPPEINER (*Chem. Centr.*, 1906, ii, 1512; from *Arch. klin. Med.*, **87**, 373—388. Compare Abstr., 1906, ii, 917).—Comparative experiments are recorded on the amount of destruction of invertase by ultra-violet light in atmospheres containing oxygen, and in the presence of gases free from oxygen, in the presence and absence of materials such as sulphites which absorb oxygen; in the presence and absence of fluorescent materials, &c. The destruction which occurs in the absence of oxygen, as, for instance, in atmospheres of hydrogen or nitrogen, is less than when oxygen is present, but is not due to the presence of traces of oxygen. The presence of oxygen is not a condition for the biological action of light. W. D. H.

Lactic Acid Fermentation. REGINALD O. HERZOG (*Zeitsch. physiol. Chem.*, 1906, **49**, 482—483).—Polemical against Buchner and Meisenheimer (Abstr., 1906, i, 919). W. D. H.

A Case of Specific Adsorption of Enzymes. SVEN G. HEDIN (*Bio-chem. J.*, 1907, **2**, 112—116).—The α- and β-proteases in ox-spleen are adsorbed in the same proportions by charcoal; kieselguhr adsorbs the former, but probably not the latter at all. W. D. H.

Influence of Temperature on the Work of the Proteolytic Enzyme and the Zymase in Killed Yeast Cells. ANNA PETRUSCHEWSKY (*Zeitsch. physiol. Chem.*, 1907, **50**, 251—262).—The experiments recorded confirm the statement that the proteolytic ferment (endotryptase) separated from yeast cells destroys zymase, and the destruction of the latter is the more complete, the more energetic the action of the former is. Zymase is not yet obtainable in a pure condition, and therefore observations on the physicochemical laws that regulate its action are not possible. The harmful action of it on endotryptase can be lessened by working at low temperatures or by the addition of strong solutions of sugar. W. D. H.

Extraction by Caseinogen of Trypsin Adsorbed by Charcoal. SVEN G. HEDIN (*Bio-chem J.*, 1907, **2**, 81—88).—A solution of caseinogen in 0·2% sodium carbonate solution extracts trypsin which has been adsorbed by charcoal. Usually in less than thirty minutes at 20° the extraction comes to an end; the final amount extracted rises with the temperature, and with the amount of caseinogen used up to a certain limit, beyond which the amount extracted is independent of the amount of caseinogen. The amount of water present makes no difference. The results support the view that proteids combine with trypsin before they are broken up by it. W. D. H.

Behaviour of Peroxydase towards Iodine. ALEXIS BACH (*Ber.*, 1907, **40**, 230—235. Compare Abstr., 1904, ii, 310).—As the oxidising action of hydrogen peroxide on hydriodic acid, aromatic amines, and phenols is increased by the presence of peroxydase from horse-raddish roots or other vegetable sources, according to the theory of specific ferment action, the peroxydase should consist of at least three enzymes. All attempts, however, either by fractional precipitation, by means of alcohol or acetone, or by destroying part of the peroxydase by means of iodine, to obtain a peroxydase incapable of increasing the activity of hydrogen peroxide towards all three classes of substances, have been unsuccessful.

The effect of iodine on the influence of peroxydase on the oxidation of phenols by hydrogen peroxide has been studied quantitatively in the case of pyrogallol. With peroxydase extract the maximum formation of purpurogallin increases to a certain extent with the amount of iodine present, diminishing on addition of larger quantities of iodine; this points to the presence of the zymogen the conversion of which into the active peroxydase is accelerated by addition of iodine. Precipitated peroxydase, on the other hand, does not contain zymogen, since its influence on the oxidation of pyrogallol by hydrogen peroxide is not increased by addition of iodine. G. Y.

Organic Chemistry.

Melting Points and Boiling Points of Aliphatic and Aromatic Hydrocarbons. Gustave Hinrichs (*Compt. rend.*, 1907, **144**, 431).—The author states that the anomalies in the melting points of fatty and aromatic hydrocarbons to which Tsakalotos has drawn attention (this vol., i, 105) have already been studied by him (Abstr., 1891, 1330, 1441; 1892, 260; 1906, i, 723). E. H.

Artificial Naphtha. K. W. Charitschkoff (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 878—880, 880—881).—Artificial naphtha was obtained by Sabatier and Senderens' method, by passing a mixture of hydrogen and acetylene over nickel shavings at 300°; the yield is very poor, a large quantity of resin being formed. The naphtha itself is a mixture resembling the decomposition products of natural naphtha, and contains a large proportion of unsaturated substances as well as some products of oxidation. The iodine numbers (*A*) and the coefficients of acidity (*B*) of various fractions are as follows:

	(1) For decomposition products.		(2) Artificial naphtha.	
	A.	*B.*	*A.*	*B.*
Up to 150°	129	0·5	237	14·05
150—200	112	1·8	189	2·81
200—270	66	1·5	124	6·1

Thus the higher the boiling point of a fraction of artificial naphtha, the less oxygen does it contain; this fact is also in accordance with the results of analysis, which shows that the residue, boiling above 270°, consists mainly of hydrocarbons and is very similar to the heavy naphtha residues and resins. All this leads to the conclusion that during the experiment various complex processes of condensation and polymerisation occur and it is probable that the complex nature of natural naphtha is also due to such reactions. Z. K.

Octanes from Rock-oil. Felix B. Ahrens (*Ber.*, 1907, **40**, 848—852).—A number of derivatives have been prepared from an oil, $C_{10}H_{18}$, b. p. 121—122°, D^{23} 0·7245, obtained from rock-oil after removal of the toluene by nitration; it solidifies to a paraffin wax-like mass in liquid air. The action of chlorine on the oil leads to the formation of mono-, di-, and tri-chloro-derivatives. The *monochloro-product*, $C_{10}H_{17}Cl$, is a colourless oil, b. p. 164—166°. The *dichloro-product*, $C_8H_{16}Cl_2$, is a yellow oil, b. p. 122—124°/49 mm. The *product* obtained by the action of bromine on the oil decomposes on distillation.

The action of nitric acid, D 1·075, on the oil leads to the formation of (*a*) hydroxy-β-methylglutaric acid; (*b*) a white, crystalline *acid*, $C_7H_{12}O_7$, m. p. 184°, and (*c*) two *nitro-octanes*.

The tert.-*nitro-octane*, $C_8H_{17}\cdot NO_2$, is a colourless liquid, b. p. 113—114°/36 mm., $D^{19\cdot5}$ 0·9671, and on reduction with tin and hydrochloric acid yields the tert.-*octylamine*, $C_8H_{17}\cdot NH_2$. This is a colourless liquid, b. p. 155—156°, $D^{22\cdot5}$ 0·8051, which has a sharp odour. The *platinichloride*, $(C_8H_{19}N)_2,H_2PtCl_6$, decomposes above 200°; the *aurichloride*, $C_8H_{19}N,HAuCl_4$, long needles, m. p. 77—79°; the picrate, $C_8H_{19}N,C_6H_3O_7N_3$, m. p. 138°. A small amount of a *picrate*, m. p. 200°, was obtained also.

The sec.-*nitro-octane* is an almost colourless liquid, b. p. 114—115°/30 mm., $D^{19\cdot5}$ 0·9342. The sec.-*base* obtained on reduction of this forms two picrates. The *picrate* crystallising from benzene in slender needles, m. p. 108°, yields colourless sec.-*octylamine*, b. p. 164—166, $D^{12\cdot5}$ 0·801, which forms a *platinichloride* decomposing above 200°, and an *aurichloride*, m. p. 41—42°. The *picrate* crystallising in yellow needles, m. p. 82—83°, yields sec.-*octylamine*, b. p. 163—164°, $D^{22\cdot5}$ 0·788; this forms a *platinichloride* crystallising in leaflets or needles and decomposing above 200°, and an *aurichloride*, yellow leaflets, m. p. 42—43°. G. Y.

Action of Nitrous Acid on *iso*Butylene. K. W. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 955—958).—The author has shown previously (*Bull. Moscow Inst. Rural Economy*, 1899, **5**, 248) that the action of nitrogen peroxide on *iso*butylene yields a liquid giving *iso*butylenediamine on reduction, and a colourless, crystalline compound, $C_4H_8O_4N_2$, m. p. 104°, which could not be reduced.

The action of an ethereal solution of nitrous acid (rather less than 1 mol. N_2O_3) on a cooled ethereal solution of *iso*butylene yields: (1) a small quantity of a *nitrosite*, $C_4H_8O_3N_2$, m. p. 80—80·2°, which crystallises in colourless, shining plates and dissolves sparingly in most of the ordinary solvents, forming blue solutions; (2) a large proportion of a blue *liquid*, of which the crystalline compound is probably a polymeride. Both compounds yield *iso*butylenediamine on reduction with tin and hydrochloric acid.

The reducibility of the nitrosite depends on the presence of the grouping $CH_2{:}C$ (compare Demjanoff, Abstr., 1899, i, 845; Schmidt, Abstr., 1903, i, 597). T. H. P.

Electrolytic Preparation of Chloroform. P. TRECHZINSKY (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 734—741).—Chloroform has been prepared by the electrolysis of calcium chloride in the presence of ethyl alcohol. Judging by the yield of chloroform, the reaction most probably proceeds in the following stages: $CH_3\cdot CH_2\cdot OH + Cl_2 \longrightarrow CH_3\cdot CHO$; $CH_3\cdot CHO + 3Cl_2 \longrightarrow CCl_3\cdot CHO$; $2CCl_3\cdot CHO + Ca(OH)_2 = 2CHCl_3 + Ca(HCO_2)_2$. This is further confirmed by the fact that when the yield of chloroform is small, the escaping gas has an odour of acetaldehyde, acetic acid, and ethyl acetate. The concentration of the calcium chloride must lie between 40 and 70 grams per 100 c.c. of water, the alcohol must be in the proportion of 5—10 c.c. per 450 c.c. of calcium chloride solution, and the temperature must lie between 49° and 73°. The voltage employed has no effect providing it is above 2·2 and the best strength of current is 8 amperes. With slight modifications potassium or sodium chloride can replace calcium chloride.

Z. K.

Action of Dilute Nitric Acid on Haloid Compounds. III. MICHAEL I. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 607—612. Compare Abstr., 1904, i, 495, 657).—The action of dilute nitric acid on *iso*butyl chloride yields: (1) *a-chloro-β-nitro-β-methylpropane* (tertiary chloronitro*iso*butane), $CH_2Cl\cdot CMe_2\cdot NO_2$, b. p. 181—183°, D_0^0 1·1960, D_0^{19} 1·1822, n_D^{19} 1·44461; reduction with tin and hydrochloric acid gives a mixture of bases including *a-chloro-β-amino-β-methylpropane*, $CH_2Cl\cdot CMe_2\cdot NH_2$, b. p. 120—130°, D_0^{18} 0·9464, n_D^{18} 1·42705; (2) a mixture of primary and secondary chloronitro*iso*butanes.

With *iso*butyl bromide, dilute nitric acid gives *a-bromo-β-nitro-β-methylpropane*, $CH_2Br\cdot CMe_2\cdot NO_2$, b. p. 110—115°/60 mm., D_0^{18} 1·5545, n_D^{18} 1·47838, and other products not yet identified.

On heating *iso*amyl chloride with nitric acid (D 1·075) in a sealed tube at 125°, it yields *a-chloro-γ-nitro-γ-methylbutane*,

$$CH_2Cl\cdot CH_2\cdot CMe_2\cdot NO_2,$$

b. p. 203—204°/735 mm., D_0^0 1·1739, D_0^{20} 1·1576, n_D^{20} 1·45412, which gives a mixture of bases when reduced with tin and hydrochloric acid.

T. H. P.

Transformation of the Primary Saturated Alcohols into the Corresponding Monobasic Acids. H. FOURNIER (*Compt. rend.*, 1907, **144**, 331—333).—Under conditions employed by previous authors, the oxidation of primary saturated alcohols by means of alkaline potassium permanganate gives very little of the corresponding monobasic acid. The author shows that if the alcohol is dissolved in a 10% solution of potash and treated gradually with a 3% solution of potassium permanganate in quantity sufficient to give 2 atoms of oxygen for each molecule of alcohol, the mixture being kept cold, the potassium salt of the corresponding monobasic acid is formed, and the latter may be liberated, after removal of manganese dioxide by filtration, by adding sulphuric acid very slowly. In this way *iso*amyl alcohol, δ-methylamyl alcohol, ε-methylhexyl alcohol, *n*-butyl alcohol, *iso*butyl alcohol, and propyl alcohol, on oxidation, give yields of the corresponding monobasic acids varying from 70—75% of the theory. Ethyl alcohol gives only a 50% yield of acetic acid.

E. H.

Certain Molecular Compounds of Calcium Chloride. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1010—1036. Compare Abstr., 1906, i, 131, 132).—The alcoholates of calcium chloride are readily obtained by dissolving anhydrous calcium chloride in dehydrated alcohols. Heat is developed and, when the solution cools, the alcoholate is deposited in crystals.

The melting point diagram of the system $CaCl_2,MeOH$ consists of three intersecting curves: (1) the solubility curve of the compound $CaCl_2,4MeOH$ reaching to 55°; (2) the solubility curve of the *compound* $CaCl_2,3MeOH$ extending from 55° to 178°, the m. p. of the compound, and (3) the solubility curve of another alcoholate containing less alcohol. The diagram greatly resembles that obtained for the system $CaCl_2,H_2O$ (Roozeboom, Abstr., 1889, 752).

The solubility curves of $CaCl_2,4MeOH$ and $CaCl_2,4H_2O$ are similar and so also are those of $CaCl_2,3MeOH$ and $CaCl_2,2H_2O$; the curve for $CaCl_2,3MeOH$ is also analogous to that for $MgBr_2,6MeOH$. Tables are given showing the solubility of $CaCl_2,4MeOH$ in methyl alcohol between 0° and 56° and of $CaCl_2,3MeOH$ between 55° and 177°.

With ethyl alcohol, calcium chloride forms only one compound, $CaCl_2,3EtOH$, m. p. 97°, which separates in large crystals; its solubility in ethyl alcohol has been determined between 0° and 97°. Compounds of analogous composition are also obtained with propyl, *iso*butyl, and *iso*amyl alcohols, but their solubilities in the corresponding alcohols could not be accurately determined, as they form very viscous solutions.

Thus the alcoholates of calcium chloride are of the general type $CaCl_2,3ROH$, and crystallise more readily than those of magnesium bromide, which have the formula $MgBr_2,6ROH$ (compare Abstr., 1906, i, 131, 132). The m. p.'s. of the two series of compounds are as follow:

$CaCl_2,3MeOH$	177°	$MgBr_2,6MeOH$	190°
$CaCl_2,3EtOH$	97°	$MgBr_2,6EtOH$	108·5°
$CaCl_2,3PrOH$	87—88°	$MgBr_2,6PrOH$	52°
$CaCl_2,3CHMe_2{\cdot}CH_2{\cdot}OH$	105°	$MgBr_2,6CHMe_2{\cdot}CH_2{\cdot}OH$	80°

With *iso*propyl alcohol, calcium chloride forms an *alcoholate*, $CaCl_2,3Pr^{\beta}OH$, crystallising in small needles, whilst with tertiary alcohols it gives alcoholates, which apparently contain only 1ROH and do not melt, but decompose, on heating.

On dissolving dehydrated calcium chloride in a dehydrated monobasic fatty acid, a crystalline compound is obtained, which can be crystallised from the corresponding acid (compare Benrath, Abstr., 1905, i, 734). In the system $CaCl_2,C_2H_4O_2$, the m. p. first falls from 16·2°, that of acetic acid, to 11·1°, which corresponds with a content of 42% of the compound $CaCl_2,4C_2H_4O_2$; it then rises to 73°, the m. p. of $CaCl_2,4C_2H_4O_2$, which crystallises in rhombohedra. The solubility curve of this compound in acetic acid is very similar to that of $MgBr_2,6C_2H_4O_2$. Formic acid dissolves calcium chloride, but deposits no compound on cooling. Propionic acid gives the *compound*,

$$CaCl_2,4C_3H_6O_2,$$

and butyric acid, $CaCl_2,C_4H_8O_2$ (?), both crystallising in leaflets.

The compound of calcium chloride with ethyl acetate, obtained by Liebig (*Annalen*, 1833, 5, 36—37), has the composition

$$CaCl_2,2CH_3{\cdot}CO_2Et,$$

and is almost insoluble in ethyl acetate. Compounds of similar constitution are $CaCl_2,2CH_3{\cdot}CO_2Me$, $CaCl_2,2H{\cdot}CO_2Et$, and

$$CaCl_2,2CH_3{\cdot}CO_2Pr\ (?).$$

With methylal, calcium chloride forms $CaCl_2,CH_2(OMe)_2$, which crystallises in small needles, insoluble in methylal, and with acetal, $CaCl_2,CH_2(OEt)_2$, which forms long leaflets. T. H. P.

Preparation of Optically Active Butyl Alcohol. **RICHARD METH** (*Ber.*, 1907, 40, 695—697).—The author describes a novel method of resolving an inactive alcohol into its optically active components, the principle of which depends on the formation of a hydrogen ester from the alcohol and a dibasic acid, the resolution of this acid-ester by the ordinary alkaloidal method and the subsequent hydrolysis of the optically active acid-ester obtained in this manner.

sec.-Butyl alcohol was converted into butyl hydrogen sulphate (compare Marckwald, Abstr., 1902, i, 418). *Barium* sec.-*butyl sulphate*, $(C_4H_9SO_4)_2Ba,2H_2O$, is readily soluble in water; the calculated amount of brucine sulphate was added to its aqueous solution, and the precipitated barium sulphate filtered off. The brucine salt of the *d*-acid was readily obtained pure from the filtrate; it has m. p. 210°, decomposing; this brucine salt was then converted into *barium* d-sec.-*butyl sulphate*, $(C_4H_9SO_4)_2Ba,H_2O$, which, in aqueous solution, has $[\alpha]_D$ +0·57° (C = 41·85). The barium salt was hydrolysed by boiling with dilute sulphuric acid for three hours; the resulting alcohol had $[\alpha]_D$ +0·32°. Partial racemisation probably occurred during the hydrolysis of the barium salt. A. McK.

Various Syntheses of Dimethyl*iso*propylcarbinol, $CMe_2Pr^\beta{\cdot}OH$. Louis Henry (*Compt. rend.*, 1907, **144**, 308—313).—The author having obtained Butleroff's pentamethylethanol (Abstr., 1875, 1248) by the action of magnesium methyl bromide on ethyl-*α*-chloro-*α*-methylpropionate, expected that under the same conditions *α*-chloro-*β*-methylpropaldehyde would give Friedel's pinacolyl alcohol, $CMe_3{\cdot}CHMe{\cdot}OH$, but obtained instead dimethyl*iso*propylcarbinol. The reaction is explained by the scheme $CMe_2Cl{\cdot}CHO \longrightarrow CMe_2Cl{\cdot}CHMe{\cdot}OMgBr \longrightarrow$

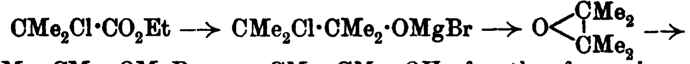
$\mathrm{O}<\begin{matrix}\mathrm{CMe_2}\\ |\\ \mathrm{CHMe}\end{matrix} \longrightarrow MgBr{\cdot}O{\cdot}CMe_2{\cdot}CHMe_2 \longrightarrow OH{\cdot}CMe_2{\cdot}CHMe_2$.

In support of this the author adduces the facts that (1) by the action of magnesium methyl bromide on Brochet's *αβ*-dichlorodi*iso*butyl ether, $CMe_2Cl{\cdot}CHCl{\cdot}O{\cdot}C_4H_9$ (*Ann. Chim. Phys.*, 1897, [vii], 10, 289 and 347), *β* chloro-*α*-methyldi*iso*butylether, $CMe_2Cl{\cdot}CHMe{\cdot}O{\cdot}C_4H_9$, b. p. 178—179° is obtained. (If the *αβ*-dichlorodi*iso*butyl ether is added to excess of magnesium methyl bromide in ethereal solution, hydrogen chloride is eliminated giving the unsaturated ether, $CMe_2{:}CMe{\cdot}O{\cdot}C_4H_9$, b. p. 162—164°.) (2) *β*-Methylbutylene-*βγ*-oxide,

$\mathrm{O}<\begin{matrix}\mathrm{CHMe}\\ |\\ \mathrm{CMe_2}\end{matrix}$ (b p. 75°), very readily gives *βγ*-dimethyl-*β*-butanol by reaction with magnesium methyl bromide in the usual way.

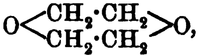
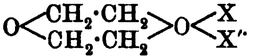
*iso*Amylene monochlorohydrin, $CMe_2Cl{\cdot}CHMe{\cdot}OH$, formed by the action of hydrogen chloride on *β*-methylbutylene oxide, also reacts with magnesium methyl bromide, giving almost entirely dimethyl*iso*propylcarbinol instead of the secondary pinacolyl alcohol expected, which, however, seems to be found in small amount. The course of the reaction must be similar to that in the case of *α*-chloro-*β*-methylpropaldehyde, since the first action of magnesium methyl bromide is to cause the evolution of methane and formation of the compound $CMe_2Cl{\cdot}CHMe{\cdot}OMgBr$.

The fact that the group $CMe_2Cl{\cdot}$, which in *α*-chloro-*β*-methylpropaldehyde is not attacked by the magnesium methyl bromide, is also present in ethyl α-chloro-α-methylpropionate from which pentamethylethanol is formed, leads to the following scheme:



$$CMe_2Cl\cdot CO_2Et \longrightarrow CMe_2Cl\cdot CMe_2\cdot OMgBr \longrightarrow O{<}\genfrac{}{}{0pt}{}{CMe_2}{CMe_2} \longrightarrow$$

$CMe_3\cdot CMe_2\cdot OMgBr \longrightarrow CMe_3\cdot CMe_2\cdot OH$, for the formation of the latter. E. H.

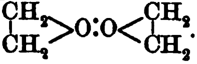
Conversion of Ethylene Glycol into Acetaldehyde. **Alexei E. Faworsky** (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 741—755).—Although the end products resulting from the action of dehydrating agents or of aqueous mineral acids on the α-glycols are well known, the actual mechanism of the reaction is purely hypothetical, owing largely to the fact that in no case have the intermediate substances been isolated. Wurtz's experiments on ethylene glycol have been repeated with slight modifications, and acetaldehyde and ethylidene ethylene ether have been obtained, but the main product was diethylene ether, a substance identical with Wurtz's dioxyethylene and Laurenço's glycolic ether. It has all the properties of an ether, and its refractive index corresponds with the formula  $O{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}O$, but it very readily forms oxonium salts with iodine, sulphuric, and picric acids of the type  $O{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}O{<}\genfrac{}{}{0pt}{}{X}{X}$. When carefully distilled with sulphuric acid or zinc chloride, the distillate consists mainly of acetaldehyde, hence diethylene ether must be taken as a true intermediate product formed by the action of these reagents on ethylene glycol, its mode of formation being exactly analogous with that of any other ether, whilst the formation of acetaldehyde and ethylidene ethylene ether is assumed to be due to the successive formation and decomposition of its oxonium salt. Contrary to Krassuski's supposition (Abstr., 1903, i, 8), it is considered very unlikely that ethylene oxide should be an intermediate compound in these reactions. The *oxonium iodide* of ethylene ether, m. p. 84°, is immediately decomposed by water and air, is soluble in benzene and chloroform which also decompose it. The *sulphate*, m. p. 100°, is dissolved and decomposed by water. The *picrate*, m. p. 66°, forms pale yellow crystals. Z. K.

Constitution of Dioxyethylene. **Emanuale Paternò** and **Rosario Spallino** (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 87—92. Compare preceding abstract).—Dioxyethylene bromide, m. p. 65°, prepared by the method given by Wurtz (*Ann. Chim. Phys.*, 1863, [iii], **69**, 321), has the formula $(C_2H_4O)_2Br_2$ in freezing benzene.

Dioxyethylene, b. p. 101°, m. p. 9°, also combines readily (1) with iodine, giving the *iodide*, $(C_2H_4O)_2I_2$, m. p. 85°; (2) with concentrated sulphuric acid, giving the *sulphate*, $(C_2H_4O)_2H_2SO_4$, m. p. 101°, and (3) with mercuric chloride, giving the *compound*, $(C_2H_4O)_2HgCl_2$, which dissolves in water, alcohol, or ether and can be crystallised.

When heated with concentrated hydriodic acid in a sealed tube at 140°, dioxyethylene yields ethyl iodide (?) and acetic acid. Oxidation with permanganate yields carbon dioxide and oxalic acid.

These results show that dioxyethylene exhibits both the behaviour of compounds containing a double linking and that characteristic of substances in which basic oxygen is present. Its constitution is most probably represented by the formula



$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!>\!O{:}O\!<\!\begin{matrix}CH_2\\|\\CH_2\end{matrix}$. T. H. P.

Preparation of Alkyloxy-glycols. Auguste Béhal and Marcel Sommelet (D.R.-P. 177615).—The alkyloxy-glycols, $OH\cdot CRR'\cdot CH_2\cdot OX$, are of importance in the synthesis of aldehydes, but hitherto they have been obtained only with great difficulty. A general method of preparation has now been devised based on the action of organomagnesium compounds either on the alkyloxy-ketones, $R\cdot CO\cdot CH_2\cdot OX$, or on the esters, $CO_2R\cdot CH_2\cdot OX$, of the alkyloxy-acetic acids.

The alkyloxy-groups do not interact providing that excess of the organomagnesium compound is avoided. One molecule of this reagent is required for the alkyloxy-ketone, $RCO\cdot CH_2\cdot OX + R'\cdot MgBr = CRR'(OMgBr)\cdot CH_2\cdot OX$, and two for the alkyloxy-acid, $OX\cdot CH_2\cdot CO_2R' + 2MgRBr = OX\cdot CH_2\cdot CRR\cdot OMgBr + MgBr\cdot OR'$. On treatment with water the additive compounds yield respectively $OH\cdot CRR'\cdot CH_2\cdot OX$ and $OH\cdot CR_2\cdot CH_2\cdot OX$.

The patent contains a table of new alkyloxy-glycols which have been thus obtained. G. T. M.

Fixation of Methyl Alcohol on Camphene and Trimethylethylene. Albert Reychler (*Bull. Soc. chim. Belg.*, 1907, 21, 71—74).—When a mixture of methyl alcohol and methyl iodide is heated in a closed tube at 120—140° during two hours, the reactions represented by the following equations occur: $MeOH + MeI = Me_2O + HI$, $MeOH + HI = H_2O + MeI$. Similarly, when a mixture of camphene, methyl iodide, and methyl alcohol is heated in a closed tube for five hours at 130—140°, methyl *iso*bornyl ether is produced. This property of acting as a catalytic agent under these conditions is not confined to hydrogen iodide, since Bertram and Walbaum have shown that acetic acid and camphene react in presence of sulphuric acid to form *iso*bornyl acetate, and similar cases are recorded by Semmler (Abstr., 1901, i, 90) and Hesse (Abstr., 1906, i, 375). When β-methyl-Δ^{β}-butylene, methyl alcohol and sulphuric acid are heated together at 95° in a closed vessel, a yield equivalent to 50% of the theoretical of the corresponding *methyl amyl ether*, b. p. 86°, is obtained. T. A. H.

Structure of Phosphorous Acid and its Derivatives. IV. The Conversion of Tervalent into Quinquevalent Derivatives of Phosphorus. Alexander E. Arbusoff (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 687—718. Compare this vol., i, 8, 174).—When the tervalent derivatives of phosphorus are acted on by water or alcohol, quinquevalent derivatives are mostly obtained. The reason for this seems to be the unsaturated character of the tervalent compounds which under certain physico-chemical conditions tend to utilise their reserve of energy and pass into a more stable form. Thus, when compounds of the type $P(OR)_3$ react with $R'X$ (where

R′ stands for hydrogen, or a fatty radicle either identical with or different from R, and X a halogen or hydroxyl), they are converted into compounds of the type $O:PR'(OR)_2$. R′X acting as a catalyst, the course of the reaction being $R'X + P(OR)_3 = PR'(OR)_3X = O:PR'(OR)_2 + XR$. Various ethyl, propyl, and methyl compounds of this character have been prepared in this way. The intermediate compounds being very unstable can seldom be isolated, but the compound $PMe(OPh)_3I$, prepared by the action of methyl iodide on triphenyl phosphite, has been obtained, and on distillation yields iodobenzene and diphenyl methyl phosphite, b. p. 201—202°/11 mm. (compare Abstr., 1898, i, 417). Thus, water or alcohol acts on phosphorus trichloride thus: $PCl_3 + 3ROH = P(OR)_3 + 3HCl$; $P(OR)_3 + HCl = P(OR)_3HCl \longrightarrow O:P(OR)_2H$, and to obtain a good yield of such a compound it is necessary (1) to remove too great an excess of hydrochloric acid which might react further and ultimately produce phosphorous acid itself, and (2) to work at low temperatures (Levitsky, Abstr., 1903, i, 733). All the reactions adduced by Levitsky in proof of the tervalency of the phosphorus in the ethyl compound of this type and in its acid are shown to be equally well explained by assuming the quinquevalency of the phosphorus which is more in accordance with its behaviour towards the copper halides. Again, when trimethyl phosphite is mixed with water, its characteristic odour vanishes immediately, great heat is developed, and the compound $O:P(OMe)_2H$ is formed; if this reaction takes place as explained above, then the fact that it is immediate and seemingly independent of the mass of the reacting substance is explained by its irreversibility, whilst the development of heat might be due to the oxygen changing from a single to a double linking with the phosphorus. Finally, the hydroxyl derivatives of tervalent phosphorus cannot exist, and when formed are at once converted into derivatives of quinquevalent phosphorus in exact analogy with $>C:CH\cdot OH \longrightarrow >CH\cdot CHO$. Z. K.

Crystalline Compound of Acetic Acid with Hydrogen Bromide. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1104—1105).—McIntosh (Abstr., 1906, i, 481) has stated that acetic acid does not unite with hydrogen bromide at low temperatures, but the author finds that, when glacial acetic acid is saturated with dry hydrogen bromide, heat is developed, and the viscous liquid obtained, when kept in a cold place, solidifies to a mass of crystals of the *compound* $2C_2H_4O_2,HBr$, m. p. 7—8°.

A similar viscous liquid is obtained on mixing glacial acetic acid with concentrated sulphuric acid, but no crystalline compound could be separated. T. H. P.

[Preparation of Bromides of Dialkylacetic Acids.] KALLE & Co. (D.R.-P. 175585).—Instead of transforming the dialkylmalonic acids into the dialkylacetic acids and then converting the latter into the dialkylacetamides, the dialkylmalonic acid may be treated directly with bromine and the bromoalkylacetic acid produced then converted into the amide. *a*-Bromo-*a*-ethylbutyric acid, $CEt_2Br\cdot CO_2H$, b. p. 200—201°, is obtained by heating diethylmalonic acid with an equal weight of bromine at 160—180°, liberating hydrogen bromide. *a*-Bromo-*a*-methylvaleric acid has b. p. 204—205°. *a*-Bromo-*a*-ethylvaleric and *a*-bromo-*a*-propylvaleric acids have b. p. 212—213° and 228—230° respectively. These acids are readily converted into the corresponding amides. G. T. M.

Theory of Saponification. II. RICHARD FANTO and MILAN J. STRITAR (*Annalen*, 1907, **351**, 332—343. Compare Abstr., 1904, i, 843).—In Geitel's method of "cold saponification" (Abstr., 1897, ii, 547) three reactions may take place: (1) formation of a soap and glycerol by saponification of the triglyceride; (2) ester formation by displacement of glycerol by the solvent alcohol, and (3) formation of a soap by hydrolysis of the ester formed intermediately. The course of these reactions must be studied before the results obtained by Geitel's method of saponification can be interpreted.

Two series of saponification experiments with rape-seed oil are described, and the results tabulated and expressed in curves. The oil is shaken with a known volume of alcoholic potassium hydroxide, the reaction stopped after a given time by addition of a measured amount of acetic acid, and, after addition of alcohol and ether, the excess of acetic acid titrated; from this is calculated the ions, OH′, taking part in the hydrolysis. An excess of acid is then added, the alcohol and ether distilled off, and the total liberated glycerol determined in the residue. The difference of the total glycerol and that corresponding with the ions, OH′, required for the hydrolysis is the amount of glycerol displaced in the ester formation. It is noticeable that the curves do not show any irregularities in the neighbourhood of the point of clearance of the hydrolysis mixture. An apparent decrease in the amount of the "ester-glycerol" must be caused by partial hydrolysis of the ester in presence of still unchanged triglyceride.

The unchanged triglyceride is isolated by distillation in a current of steam (Henriques, Abstr., 1899, ii, 258) and successive extraction of the residue with light petroleum and alcohol; when hydrolysed with alcoholic potassium hydroxide, the residual triglyceride of rape-seed oil yields erucic and arachidic acids. From the quantitative results obtained, the conclusion is drawn that the saturated triarachin is more stable towards alkalis than the unsaturated trierucin and trirapin.

G. Y.

Catalytic Hydrogenation of Unsaturated Esters. GEORGES DARZENS (*Compt. rend.*, 1907, **144**, 328—331).—The author has applied to unsaturated esters the method of hydrogenation in the presence of nickel obtained by reducing the oxide at 280° (Abstr., 1905, i, 172). Ethyl acrylate and dimethylacrylate give ethyl propionate and *iso*valerate respectively. Ethyl pelargonate is obtained from ethyl Δ^{β}-nonenoate, while the series of $\beta\beta$-methylalkylacrylic esters of the type $CMeR\colon CH\cdot CO_2Et$ give the homologous fatty acid esters of the general formula $CHMeR\cdot CH_2\cdot CO_2Et$. The disubstituted acrylic esters were obtained by condensing the ketones, $R\cdot COCH_3$, with ethyl chloroacetate, and dehydrating the β-hydroxy-acid formed, by means of phosphoric oxide. Ethyl undecenoate,

$$CH_2{:}CH\cdot[CH_2]_8\cdot CO_2Et,$$

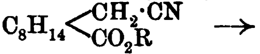
prepared by distilling castor oil in a vacuum, gives ethyl undecoate. Ethyl cinnamate and ethyl phenylcrotonate give ethyl phenylpropionate and ethyl phenylbutyrate. $\Delta^{1:2}$-*cyclo*Hexenecarboxylic acid is obtained from *cyclo*hexanone. The bisulphite compound of this ketone is treated with potassium cyanide, and the nitrile obtained is hydrolysed by cold hydrochloric acid, forming hydroxy*cyclo*hexanecarboxylic acid of which the ethyl ester after dehydration by phosphoric oxide gives ethyl $\Delta^{1:2}$-*cyclo*hexenecarboxylate by hydrogenation. The *o*-, *m*-, and *p*-methyl homologues of this acid are similarly prepared. In the same manner hexahydrophenylacetic acid is obtained from *cyclo*hexanone after condensing the latter with ethyl chloroacetate.

The method of catalytic hydrogenation differs from Bouveault and Blanc's method, using sodium and boiling alcohol (Abstr., 1903, i, 597, 673; 1904, i, 642; 1905, i, 11, 12, 13), in that the latter transforms the group $-CO_2K$ into $-CH_2\cdot OH$, and often hydrogenates the aromatic nucleus and the ethylenic grouping in the αβ-position, while catalytic hydrogenation does not affect the CO_2H group or the aromatic nucleus unless it is partially hydrogenated already, and reduces the ethylenic grouping in all positions.

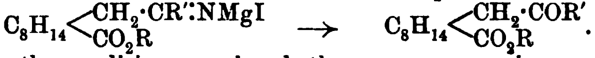
The reactions give a practical method for the synthesis of an acid, C_{n+2}, from an aldehyde or ketone C_n. E. H.

Preparation of Acylcampholic Esters and a New Method of Formation of Hydroxyphenylhomocampholic Acid.

ALBIN HALLER and CHARLES WEIMANN (*Compt. rend.*, 1907, **144**, 297—301. Compare Haller, Abstr., 1889, 1205; Blaise, Abstr., 1901, i, 133).—When organomagnesium compounds act on the cyanocampholic esters, imino-compounds are formed, and these are hydrolysed by dilute sulphuric acid into keto-derivatives,



$$C_8H_{14}<\begin{matrix}CH_2\cdot CN\\ CO_2R\end{matrix} \longrightarrow$$



$$C_8H_{14}<\begin{matrix}CH_2\cdot CR'{:}NMgI\\ CO_2R\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH_2\cdot COR'\\ CO_2R\end{matrix}.$$

Under the conditions employed, the organomagnesium compound does not attack the group $\cdot CO_2R$. The esters so obtained are very difficult to saponify, and as they resemble in this respect the β-camphoric esters they probably contain the $\cdot CO_2R$ group in a similar position in the molecule. Their ketonic nature is proved by the formation of semicarbazones. *Methyl acetylcampholate*,

$$CO_2Me\cdot C_8H_{14}\cdot CH_2\cdot COMe,$$

is an oil with an agreeable odour, almost colourless when freshly distilled, b. p. 190°/50 mm., $[\alpha]_D$ +73·29°; the *semicarbazone*, $C_{14}H_{25}O_3N_3$, forms white needles, m. p. 251°. *Ethyl propionylcampholate*, $CO_2Et\cdot C_8H_{14}\cdot CH_2\cdot COEt$, is an oil, b. p. 198°/25 mm., slightly yellow when freshly distilled, and becoming distinctly yellow on contact with light and air; the *semicarbazone*, $C_{16}H_{29}O_3N_3$, forms silky needles, m. p. 180·5°. *Methyl benzoylcampholate*, $CO_2Me\cdot C_8H_{14}\cdot CH_2\cdot COPh$, crystallises from light petroleum in spangles, m. p. 71°; its *semi-*

carbazone has m. p. 222°. The *ethyl* ester has m. p. 48—49°, b. p. 225°/15 mm.; its *semicarbazone* has m. p. 180°. *Benzoylcampholic acid*, $CO_2H\cdot C_8H_{14}\cdot CH_2\cdot COPh$, which is the keto-derivative corresponding with hydroxyphenylhomocampholic acid,

$$CO_2H\cdot C_8H_{14}\cdot CH_2\cdot CHPh\cdot OH$$

(Haller and Minguin, Abstr., 1900, i, 452), is obtained by heating the ester with hydrochloric acid in a sealed tube to 120—225° for five days. The product is insoluble in concentrated, but soluble in dilute, potassium hydroxide, from solution in which it is thrown down by acids as a white, flocculent precipitate, which crystallises from alcohol or ether in needles, m. p. 163°, $[\alpha]_D$ + 69°28′ (in methyl alcohol). The *semicarbazone*, $C_{18}H_{25}O_3N_3$, has m. p. 210° (partial decomp.). On reduction with sodium amalgam the acid gives hydroxyphenylhomocampholic acid, which crystallises from methyl alcohol in white, transparent lamellæ containing methyl alcohol of crystallisation; it loses the alcohol at 130° and then melts at 200—202°. The acid obtained by the hydrolysis of benzylidenecamphor (Haller and Minguin, *loc. cit.*) behaves in exactly the same manner, and a mixture of the two products has m. p. 200—202°. It follows that the representation of hydroxyphenylhomocampholic acid as an ε-hydroxy-acid is correct.

E. H.

Some Derivatives of Dehydrocampholenic Acid. MICHAEL N. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 718—721).—In order to explain the structure of some nitro-derivatives of camphene, it was found necessary to investigate some derivatives of dehydrocampholenic acid, $C_{10}H_{14}O_2$. The *sodium* and *silver* salts were analysed. The *chloroanhydride*, $C_{10}H_{13}OCl$, is prepared by dissolving the perfectly dry acid in an excess of phosphorus trichloride; b. p. 116—117°/15 mm., 229—230°/745 (slight decomp.), m. p. 37·5—38·5°. Cold alcohol converts it into the *ethyl* ester, $C_{10}H_{13}O_2Et$, which distils with slight decomposition under the ordinary pressure, $D_0^{16\cdot5}$ 1·0215, $n_D^{16\cdot5}$ 1·47446. By saturating the chlorine compound with ammonia, the *amide*, $C_{10}H_{13}O\cdot NH_2$, is obtained, and crystallises from alcohol in thin, long prisms, m. p. 114·5—115·5°. The chemical and physical properties of the derivatives both point to the saturated character of campholenic acid. Z. K.

The van't Hoff-Wislicenus Configuration Theory. ARTHUR MICHAEL (*J. pr. Chem.*, 1907, [ii], **75**, 105—120).—A reply to Lossen (Abstr., 1906, i, 796) and a general criticism of Wislicenus's views on stereochemical structure. G. Y.

Ethyl Lactyl-lactate. ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1907, **144**, 425—427).—From the product of heating pure ethyl lactate in a sealed tube at 250° for seven to eight hours, there were isolated ethyl alcohol, ethyl lactate, and *ethyl lactyl-lactate*, $OH\cdot CHMe\cdot CO\cdot O\cdot CHMe\cdot CO_2Et$, a colourless liquid with an ethereal odour, b. p. 215—220°, D_0^0 1·096. A cryoscopic determination in benzene solution gives the molecular weight 199 (theory 192); it seems to be identical with the monoethyl dilactate of Wurtz and Friedel (*Ann. Chim. Phys.*, 1861, [iii], 63, 112). Alkalis resolve it into lactic acid. The formation of ethyl alcohol and ethyl lactyl-lactate is explained by the reaction $OH\cdot CHMe\cdot CO_2Et + OH\cdot CHMe\cdot CO_2Et = EtOH + OH\cdot CHMe\cdot CO_2\cdot CHMe\cdot CO_2Et$, which being reversible, attains an equilibrium. The reverse reaction is rapid, mere dissolution of ethyl lactyl-lactate in ethyl alcohol giving a mixture not precipitable by water. Ethyl lactyl-lactate is much more stable than the corresponding acid, which cannot be transformed directly into either salt or ester.

A fourth product of the reaction is *dl*-dilactide. Its formation is due to the elimination of a molecule of ethyl alcohol from the ethyl lactyl-lactate; this reaction also is reversible and when the alcohol is lost during rectification the proportion of dilactide increases.

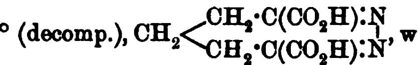
The explanation given of the formation of ethyl lactyl-lactate and dilactide is confirmed by the results of the following experiments. (1) When, after heating the ethyl lactate in a sealed tube at 260° the ethyl alcohol formed is distilled off and the residue again heated under the same conditions, the yield of ethyl lactyl-lactate is increased to an amount equivalent to half the ethyl lactate used. (2) When ethyl lactate is heated under the same conditions with an equal volume of ethyl alcohol, no trace of ethyl lactyl-lactate can be isolated from the product.

Thus the products of the action of heat on ethyl lactate are in character analogous to those obtained from lactic acid itself (Abstr., 1906, i, 333), but the mechanism of the changes is different.

E. H.

The Pyran Series. V. αε-Diketopimelic Acids. Edmond E. Blaise and Henri Gault (*Bull. Soc. Chim.*, 1907, [iv], 1, 75—95. Compare this vol., i, 147, 148).—A *résumé* of the properties of these acids has already been given (Abstr., 1906, i, 300) and their method of formation is also dealt with in this vol., i, 181.

αε-Diketopimelic acid, $CH_2[CH_2\cdot CO\cdot CO_2H]_2$, m. p. 127°, crystallises from hot acetic acid or from a mixture of this with ether or from ethyl acetate on addition of benzene. The *sodium* salt crystallises from a mixture of water and alcohol. The *methyl* ester separates from a mixture of ether and light petroleum in crystals, m. p. 62°, and furnishes a *disemicarbazone*, m. p. 250—251° (decomp.), which crystallises from a mixture of formic acid and alcohol. The *ethyl* ester furnishes a crystalline *disemicarbazone*, m. p. 250°, a *diphenylhydrazone*, m. p. 147°, which crystallises from dilute alcohol in yellow needles, and a crystalline *dioxime*, m. p. 144°. *αε-Diketopimelic anhydride*, obtained by heating the acid with acetyl chloride, could not be isolated in a pure state; with aniline it forms the *dianilide* of the acid, m. p. 192—193°, which crystallises from boiling benzene. αε-Diketopimelic acid yields a *disemicarbazone*, m. p. about 210° (decomp.), which crystallises with $2H_2O$ from boiling water. The *diphenylhydrazone*, m. p. 130° (decomp.), separates from dilute alcohol in yellow needles.

With hydrazine acetate the acid furnishes the corresponding *azine*, m. p. 210° (decomp.),  $CH_2<\begin{matrix}CH_2\cdot C(CO_2H):N\\ CH_2\cdot C(CO_2H):N\end{matrix}$, which forms small needles from dilute alcohol. The three foregoing substances are soluble in an aqueous solution of potassium hydrogen carbonate. The *dioxime*, obtained by treating the acid with hydroxylamine hydrochloride, is crystalline, m. p. 175° (decomp.), and when boiled with water furnishes glutaronitrile, b. p. 162°/25 mm. (compare Perkin, Trans., 1889, **55**, 702). On reduction with sodium amalgam, αε-diketopimelic acid furnishes the corresponding *αε-dihydroxypimelic acid*, which was not obtained pure. This on further treatment with phosphorus and hydriodic acid is converted into pimelic acid.

αε-Diketo-β-methylpimelic acid, m. p. 140° (decomp.), obtained by the hydrolysis of ethyl ethylidenebisoxalacetate, crystallises from ethyl acetate. The *methyl* ester has b. p. 172—176°/15 mm. The *dianilide*, m. p. 135°, crystallises from boiling alcohol. The *disemicarbazone*, m. p. 210° (decomp.), crystallises from boiling water. The *dioxime*, obtained by the action of hydroxylamine hydrochloride on the acid, is crystalline and, on solution in boiling water, furnishes *β-methylglutaronitrile*, b. p. 140°/10 mm., the latter on hydrolysis with potassium hydroxide in alcohol yields β-methylglutaric acid the *anilide* of which, m. p. 117°, crystallises from benzene.

αε-Diketo-β-ethylpimelic acid is obtained only in small quantities by the acid hydrolysis of ethyl propylidenebisoxalacetate and is better prepared by boiling the corresponding dianhydride with water. It crystallises from ethyl acetate and has m. p. 140° (decomp.). The *methyl* ester, m. p. 86°, obtained by heating propylidenebisoxalacetic dianhydride with methyl alcohol, crystallises from a mixture of ether and light petroleum. The *dianilide*, m. p. 114°, crystallises from dilute alcohol and is insoluble in potassium hydrogen carbonate solution. The *disemicarbazone*, m. p. about 210° (decomp.), crystallises from a mixture of chloroform and alcohol. The *dioxime* is crystalline and like its homologues is unstable, being converted by heating at 170°, or by boiling its aqueous solution, into β-ethylglutaronitrile, b. p. 144°/12 mm. This on treatment with potassium hydroxide in alcohol furnishes β-ethylglutaric acid, which is converted by boiling with acetic anhydride into *β-ethylglutaric anhydride*, b. p. 158°/13 mm., and this furnishes the corresponding crystalline *anilide*, m. p. 110°.

*αε-Diketo-β-*n*-hexylpimelic acid*, obtained by the hydration of heptylidenebisoxalacetic dianhydride, crystallises with $2H_2O$, which it retains after recrystallisation from benzene. The *methyl* ester, b. p. 206°/10 mm., is obtained by the action of methyl alcohol on heptylidenebisoxalacetic dianhydride. The *dianilide*, m. p. 104°, crystallises from dilute alcohol. The *disemicarbazone* crystallises with $2H_2O$ from a mixture of alcohol and chloroform. The *dioxime*, m. p. 180° (decomp.), forms small needles from benzene and, when its aqueous solution is boiled, passes into *β-hexylglutaronitrile*, b. p. 180°/14 mm. This, on treatment with potassium hydroxide in alcohol, yields the corresponding *acid*, m. p. 37—38°, which crystallises from a mixture of benzene and light petroleum, cooled in ice and salt.

*β-*n*-Hexylglutaric anhydride*, b. p. 194°/12 mm., obtained by boiling the acid with acetic anhydride, is a viscous liquid at the atmospheric temperature, but separates from methyl chloride in crystals. The *anilide*, m. p. 73°, crystallises from benzene. T. A. H.

Preparation of Fatty, Aromatic, and Hydroaromatic Aldehydes. AUGUSTE BÉHAL and MARCEL SOMMELET (D.R.-P. 177614. Compare this vol., i, 275).—On heating the alkyloxy-glycols, $OH\cdot CRR\cdot CH_2\cdot OX$, with acids the alcohol, $X\cdot OH$, is eliminated and the aldehyde, $CHRR'\cdot CHO$, is obtained. The method seems to be quite general, the alkyloxy-glycols being heated either with 20% sulphuric acid or dehydrated oxalic acid. The patent contains a table of certain aldehydes obtained by this process. G. T. M.

Compounds of Thiosulphuric Acid with Aldehydes. II. OTTO SCHMIDT (*Ber.*, 1907, **40**, 865—873. Compare Abstr., 1906, i, 711).—The existence of formaldehydethiosulpuric acid in a solution containing the two constituents is indicated by the following experiments.

If the reaction can be represented by $OH\cdot CH_2\cdot S_2O_3H \rightleftarrows CH_2O + H_2S_2O_3$, then $c/c'c'' = k$ (where c, c', and c'' are the concentrations of the three substances in the order given); for a given initial value of c'', c must increase with c', and consequently c'' must diminish. This is the case; as the concentration of the formaldehyde increases, that of the thiosulphuric acid, as measured by the time required for the separation of sulphur in the presence of hydrochloric acid, diminishes.

Regarded as $CH_2(OH)_2 + H_2S_2O_3 \rightleftarrows OH\cdot CH_2\cdot S_2O_3H + H_2O$, the reaction is one of ester-formation, and should be favoured by mineral acids; hydrochloric acid does indeed increase very markedly the stability of the formaldehydethiosulphuric acid. Thus a solution containing 47 c.c. of $N/1$ sodium thiosulphate, 3 c.c. of water, 10 c.c. of 39·95% formaldehyde, and 5 c.c. of 25% hydrochloric acid remains clear until after prolonged boiling, trithioformaldehyde is deposited in accordance with the equations: (i) $OH\cdot CH_2\cdot S_2O_3H = CH_2S + H_2SO_4$; (ii) $3CH_2S = (CH_2S)_3$.

In dilute solution the reaction (ii) does not take place, and (i) becomes reversible, the k value, calculated for a unimolecular reaction, exhibiting a fairly constant value.

The presence of formaldehyde does not influence appreciably the oxidation of sodium thiosulphate by iodine, but the velocity of oxidation of the free acid is retarded enormously in the presence of the aldehyde; in fact, the velocity is retarded under any of the conditions which favour the formation of formaldehydethiosulphuric acid, such as an increase of the concentration of the formaldehyde or of the hydrochloric acid, or of the total concentration.

C. S.

Action of Aluminium Alkyloxides on Aldehydes. Ester-condensation as a New Form of Aldehyde-condensation. VETCHESLÁV E. TISTSHENKO (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 482—540).—The reaction between aluminium propoxide and propaldehyde is similar to that between aluminium ethoxide and acetaldehyde, the principal product being propyl propionate, b. p.

122—124°/769 mm. The following compounds are also formed: (1) parapropaldehyde, b. p. 172—173°/773 mm., D^{0}_{0} 0·9643, D^{0}_{4} 0·9641, D^{20}_{0} 0·9443, D^{20}_{4} 0·9441 (compare Reformatsky, *J. Russ. Phys. Chem. Soc.*, 1890, **22**, 197); (2) hexylene glycol propionate,

$$OH\cdot CHEt\cdot CHMe\cdot CO\cdot OPr;$$

(3) propyl β-hydroxy-α-methylvalerate, resulting from the condensation of the aldehyde according to the equations: $2Et\cdot CHO = OH\cdot CHEt\cdot CHMe\cdot CHO$; $OH\cdot CHEt\cdot CHMe\cdot CHO + Et\cdot CHO = OH\cdot CHEt\cdot CHMe\cdot CH_2\cdot O\cdot COEt = OH\cdot CHEt\cdot CHMe\cdot CO\cdot OPr$. Part of the propaldol formed decomposes into an unsaturated aldehyde, which was only yielded in small quantity and was not separated, and water, which acts on the aluminium propoxide, giving propyl alcohol, $Al(OPr)_3 + 3H_2O = Al(OH)_3 + 3PrOH$.

Under the action either of potassium carbonate, as solid or saturated aqueous solution, or of dilute aqueous or alcoholic sodium hydroxide in the cold, *iso*butaldehyde gives *iso*butaldol, $2CHMe_2\cdot CHO = CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO$. When, however, potassium hydroxide at ordinary or high temperatures, or sodium acetate at 180°, is used, the aldol is accompanied by octylene glycol *iso*butyrate or its products of hydrolysis. With aluminium *iso*butoxide and *iso*butaldehyde, the principal product of condensation is *iso*butyl *iso*butyrate, b. p. 147—149°, $2CHMe_2\cdot CHO = CHMe_2\cdot CO\cdot O\cdot CH_2\cdot CHMe_2$. Products yielded in smaller proportion are: (1) *iso*butyl alcohol, and (2) octylene glycol *iso*butyrate, which is formed from the aldehyde by way of *iso*butaldol: $2CHMe_2\cdot CHO = CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO$;

$$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO + CHMe_2\cdot CHO =$$

$CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot O\cdot CO\cdot CHMe_2$. The formation of *iso*butyl alcohol may be due to the decomposition of the aluminium *iso*butoxide, thus, $Al(OC_4H_9)_3 = Al(OH)_3 + CMe_2{:}CH_2$, the aluminium hydroxide then reacting as follows: $Al(OC_4H_9)_3 + Al(OH)_3 = Al_2O_3 + 3C_4H_9\cdot OH$ or $3CHMe_2\cdot CH_2\cdot O\cdot CO\cdot CHMe_2 + Al(OH)_3 = 3C_4H_9\cdot OH + Al(C_4H_7O_2)_3$.

The action of potassium hydroxide or carbonate on ordinary *iso*valeraldehyde gives: (1) the aldol and the unsaturated aldehyde corresponding with β-methylbutaldehyde; (2) the aldol and decylene glycol *iso*valerate, derived from the α-methylbutaldehyde; there may also be formed decylene glycol from the hydrolysis of the *iso*valerate, and a substance, $C_{20}H_{38}O_3$, resulting from the dehydration of the aldol. The condensation of *iso*valeraldehyde and aluminium *iso*amyloxide gives mainly *iso*amyl *iso*valerate, small quantities of amyl alcohol, *iso*amyl hydroxydecoate, the two decylene glycol *iso*valerates and other compounds being obtained.

[With A. ALEXANDROFF.]—The only compound separated from the condensation products of aluminium ethoxide and heptaldehyde was *heptyl heptylate*, $C_6H_{13}\cdot CO_2\cdot C_7H_{15}$, b. p. 276·5—278·5° or 157·5—158·5°/24 mm., which gives the normal molecular weight in freezing benzene.

[With A. A. GRIGORIEFF.]—Aluminium ethoxide reacts with chloral or bromal in benzene solution, giving as principal product trichloroethyl trichloroacetate, $CCl_3\cdot CO_2\cdot CH_2\cdot CCl_3$, or tribromoethyl tribromoacetate.

[With M. N. Wischniakoff.]—The principal product of the reaction between aluminium ethoxide and α-bromo*iso*butaldehyde is *α-bromoiso-butyl-α-bromoisobutyrate*, $CMe_2Br{\cdot}CO_2{\cdot}CH_2{\cdot}CMe_2Br$, b. p. 114—117°/8·5 mm., which yields αβ-dibromo-αα-dimethylethane and α-bromo*iso*butyric acid when heated with hydrobromic acid in a sealed tube at 140°. Ethyl α-bromo*iso*butyrate is probably also formed.

[With N. N. Sum.]—m-*Nitrobenzyl* m-*nitrobenzoate*,

$$NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

obtained by the interaction of aluminium ethoxide and *m*-nitrobenzaldehyde, separates from benzene in small, yellow crystals, m. p. 143—144°, dissolves readily in chloroform and sparingly in other solvents and has the normal molecular weight in boiling benzene. Hydrogen bromide decomposes the ester into *m*-nitrobenzyl bromide and *m*-nitrobenzoic acid.

[With M. Gushoff.]—o-*Nitrobenzyl* o-*nitrobenzoate* (?), prepared by the action of aluminium ethoxide on *o*-nitrobenzaldehyde, separates from benzene in nodular masses of small crystals, m. p. 104—106°. p-*Nitrobenzyl* p-*nitrobenzoate*, $NO_2{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, obtained by the interaction of aluminium ethoxide and *p*-nitrobenzaldehyde in benzene solution, separates from benzene in pale yellow crystals, m. p. 171—172°, dissolves sparingly in water, alcohol, ether, light petroleum, and other ordinary solvents, and is resolved into *p*-nitrobenzoic acid and *p*-nitrobenzyl bromide by hydrogen bromide; this ester is apparently accompanied by ethyl *p*-nitrobenzoate.

Attempts to investigate the reaction between aluminium alkyloxides and unsaturated aldehydes, such as acraldehyde, crotonaldehyde, and cinnamaldehyde, gave no definite results, owing to the readiness with which these aldehydes are resinified or oxidised by the aluminium alkoxide.

The reactions of the saturated aliphatic and aromatic aldehydes with aluminium alkyloxides are hence similar to those occurring with alkalis, except that in the latter case the esters formed undergo hydrolysis to the corresponding acids and alcohols. In the conversion of aldehydes into esters by this means, the aldehyde groups, but not the radicles, combined with them, take part. This reaction does not, however, take place with esters of formic acid which contain the CHO group, nor with ketones, nor with acetal or paraldehyde. The reaction occurs with aluminium alkyloxides derived from secondary and tertiary, as well as primary, acids. The alkyloxides of sodium, magnesium, or zinc also bring about this reaction, but those of acid-forming elements, such as boron, do not do so.

The author is of opinion that none of the various hypotheses put forward to explain the action of alkalis or alkyloxides on aldehydes is sufficient to account for the facts. No conversion of ester into aldehyde has yet been observed. T. H. P.

Action of Magnesium Amalgam on *iso*Butaldehyde. Vetcheslav E. Tistshenko and G. N. Grigoreeff (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 540—547).—The fact that the action of sodium on *iso*butaldehyde yields octylene glycol *iso*butyrate and a small proportion of *iso*butyl alcohol was explained by Lederer (Abstr., 1901, i, 669) as due to the action of the moisture of the air on the sodium giving sodium hydroxide and hydrogen, the latter then reducing the aldehyde to the alcohol. To test the accuracy of this explanation, the authors replace the sodium by magnesium amalgam, which, with the moisture of the air, forms magnesium hydroxide, a compound incapable of forming either aldol or ester at the ordinary temperature; *iso*butyl alcohol should thus form the sole product of the reaction.

The action of 4 grams of magnesium in the form of amalgam on 100 grams of *iso*butaldehyde yields *iso*butyl alcohol, *iso*butyl *iso*butyrate, octylene glycol mono- and di-*iso*butyrates, the *iso*butyl ester of the acid, $C_8H_{16}O_3$ (compare Brauchbar, Abstr., 1897, i, 137), the *iso*butyrin of *iso*butyl hydroxyoctoate (?) and octylene glycol. The same products are obtained by the action of aluminium ethoxide on acetaldehyde.

The conclusion is drawn that the first change occurring in the action of magnesium amalgam on *iso*butaldehyde is represented by: $2CHMe_2\cdot CHO + Mg = CHMe_2\cdot CO\cdot Mg\cdot O\cdot CH_2\cdot CHMe_2$ or $4CHMe_2\cdot CHO + 2Mg = (CHMe_2\cdot CO)_2Mg + (CHMe_2\cdot CH_2\cdot O)_2Mg$. The subsequent actions taking place are given by the equations: $2CHMe_2\cdot CHO = CHMe_2\cdot CO\cdot O\cdot CH_2\cdot CHMe_2$; $2CHMe_2\cdot CHO = CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO$; $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO + CHO\cdot CHMe_2 =$ either $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot O\cdot CO\cdot C_3H_7$ or $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot CO\cdot O\cdot C_4H_9$.

T. H. P.

Action of Magnesium Amalgam on Acetaldehyde. M. P. VORONKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 547—550).—The results described in the preceding abstracts are not in accord with those of Meunier (Abstr., 1902, i, 335), who obtained βγ-dihydroxybutane by the action of magnesium amalgam on acetaldehyde, the latter being reduced in the same way as acetone is reduced to pinacone or benzaldehyde to hydrobenzoin by means of sodium amalgam.

The author was unable to obtain βγ-dihydroxybutane by the gradual addition of magnesium amalgam to cooled acetaldehyde, the products formed being aldol, crotonaldehyde, and β-butylene glycol acetate. The last-named compound is formed by the condensation of the aldol with the aldehyde: $OH\cdot CHMe\cdot CH_2\cdot CHO + CH_3\cdot CHO = OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH_3$. The condensing agent causing this reaction is probably a magnesium alkyloxide formed by the action of the magnesium amalgam on the aldehyde: $4CH_3\cdot CHO + 2Mg = (CH_3\cdot CO)_2Mg + Mg(OEt)_2$ or $2CH_3\cdot CHO + Mg = CH_3\cdot CO\cdot Mg\cdot OEt$.

T. H. P.

Halogen Derivatives of Acetaldehyde. PAUL FREUNDLER (*Bull. Soc. Chim.*, 1907, [iv], 1, 66—71. Compare Abstr., 1905, i, 326).—When paraldehyde is treated with bromine at −10° to −5°, it is transformed almost completely into bromoacetaldehyde. If the temperature is then allowed to rise above 0° the liquid becomes milky, develops heat, and finally separates into two layers, the upper consisting of dilute hydrobromic acid and the lower of αγ-dibromocrotonaldehyde. The latter is unstable and cannot be readily isolated, but on treatment with excess of bromine is converted into the stable ααβγ-tetrabromobutaldehyde. The initial reaction depends on the presence of some acetaldehyde in the paraldehyde used, and the further depolymerisation of the latter is brought about by the hydrogen bromide liberated.

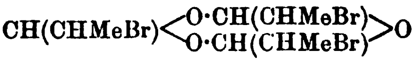
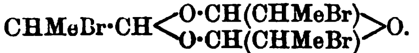
The chlorination of paraldehyde is not strictly analogous with the bromination. Chlorine is absorbed below 0°, but no reaction appears to occur below 20°. At this point chloroacetaldehyde is formed and reacts with some acetaldehyde, yielding α-chlorocrotonaldehyde which then absorbs chlorine, forming ααβ-trichlorobutaldehyde (compare Pinner, Abstr., 1876, i, 552, 553; Lieben and Zeisel, Abstr., 1883, 963, and Natterer, *ibid.*, 964). In the course of the chlorination some oxidation also occurs with the formation of acid products, and in addition a small quantity of chloral is produced.

Chloroacetal may be prepared from paraldehyde by a method similar to that adopted for bromoacetal (compare Freundler and Ledru, Abstr., 1905, i, 326). T. A. H.

Trimethylacetaldehyde [αα-Dimethylpropaldehyde]. MAXIMILIAN SAMEC (*Annalen*, 1907, 351, 255—262).—The reactions of αα-dimethylpropaldehyde have not been studied in consequence of the difficulty of its preparation. It is proposed to work out a convenient method of preparation. In the meantime the author has succeeded in obtaining the aldehyde in a 45% yield by oxidation of *tert*-butylcarbinol, which is prepared in a 4% yield, together with *iso*butylene and other hydrocarbons by Grignard's reaction from *tert*-butyl bromide, magnesium, and paraformaldehyde below 15°.

Oxidation of the alcohol with sodium dichromate and sulphuric acid leads to the formation of αα-dimethylpropaldehyde, b. p. 174°, methyl *iso*propyl ketone, b. p. 93° (Schindler, Abstr., 1893, i, 71), and ββ-dimethylpropyl αα-dimethylpropionate, b. p. 165° (Tisner, Abstr., 1891, 998). G. Y.

Action of Bromine on Polymeric Aldehydes. ADOLF FRANKE (*Annalen*, 1907, 351, 421—425. Compare Abstr., 1900, i, 427).—The reaction studied previously with para*iso*butaldehyde has been extended now to parapropaldehyde.

The action of 1 mol. of bromine on 1 mol. of parapropaldehyde in carbon disulphide solution, cooled with ice and salt, leads to the formation of two *parabromopropaldehydes*, $(C_3H_5OBr)_3$. Of these, one separates from alcohol as a white, crystalline powder, m. p. 112·5°, resembles parabromo*iso*butaldehyde, does not react with boiling water or reduce ammoniacal silver or Fehling's solution, and at 160° decomposes into the monomolecular α-bromopropaldehyde (Nef, Abstr., 1905, i, 6). The second isomeride, which is obtained from the alcoholic mother liquors, crystallises in prisms, m. p. 65°, and yields α-bromopropaldehyde when heated. These substances are considered to be probably *cis-* and *trans*-isomerides,  $CH(CHMeBr){<}\begin{matrix}O\cdot CH(CHMeBr)\\ O\cdot CH(CHMeBr)\end{matrix}{>}O$ and  $CHMeBr\cdot CH{<}\begin{matrix}O\cdot CH(CHMeBr)\\ O\cdot CH(CHMeBr)\end{matrix}{>}O$.

The action of bromide on paraldehyde leads to the formation of a *product*, m. p. about 85°. G. Y.

Preparation of Aldol and Crotonaldehyde. VICTOR GRIGNARD and JEAN REIF (*Bull. Soc. Chim.*, 1907, [iv], 1, 114—117).—To a mixture of equal weights of ether and acetaldehyde, cooled to 0°, a solution of sodium sulphite is added in small quantities at a time and the mixture is vigorously and continuously agitated, the temperature being maintained between 5° and 10° until all the sulphite solution has been added. The temperature is then allowed to rise gradually to 32°. The ethereal layer is separated, washed with sodium hydrogen carbonate solution, dried over calcium chloride, and the ether removed by distillation below 60°; the residue is nearly pure aldol, and on distillation at 84—85° furnishes crotonaldehyde, which may be purified by treatment with calcium chloride and redistillation. The yield is about 48—50% of the theoretical, the loss being due mainly to the volatility of the acetaldehyde, a defect which is not remedied by the use of a reflux condenser. T. A. H.

Some Molecular Combinations of Metallic Halides with Organic Compounds. VICTOR THOMAS (*Compt. rend.*, 1907, **144**, 376—378. Compare Bodroux, Abstr., 1902, ii, 391).—The catalytic effect of certain liquids on the reaction between iodine and the metals magnesium and aluminium is not due to the solvent action of the liquid for iodine, since some liquids, such as benzene, carbon disulphide, chloroform, and carbon tetrachloride, which readily dissolve iodine, are inactive. The aliphatic ketones, such as acetone, methyl ethyl ketone, diethyl ketóne, butyrone, and ethyl amyl ketone, the diketones, such as acetylacetone and acetonylacetone, and the aliphatic nitriles, such as acetonitrile, propionitrile, and butyronitrile, react as readily as do ether or anhydrous alcohol. But the aromatic ketones, the aldehydes, except benzaldehyde, and the aromatic nitriles are inactive.

In some cases the reaction with magnesium is so violent that the heat developed renders the mixture red hot and probably causes the formation of magnesium carbide, as on treatment with water the mass gives acetylene. With aluminium, the mixture rapidly becomes incandescent with formation of alumina, owing to the combustion of the iodide formed. The heat developed is so great that the mixture can be used to start the combustion of aluminium in alumino-thermic reactions.

In all these reactions the catalyst appears to be of a chemical order, and the combination is due to formation of an additive compound of the iodide and the solvent. A compound of magnesium iodide and alcohol very probably exists (compare Simon, Abstr., 1880, 310). Ketones and nitriles are known to combine easily with iodides.

The experiments with magnesium were effected by the gradual addition of the theoretical quantity of iodine necessary to form magnesium iodide to powdered magnesium contained in a flask and covered with excess of the different ketones and nitriles. The reaction is very violent at first, but slackens rapidly and is completed on a water-bath. From acetone a yellow, crystalline substance, $COMe_2,MgI_2$, is obtained; it is stable in air, but very easily loses iodine on warming, and is decomposed by water, half the magnesium being precipitated as magnesia and the remainder going into solution. Other ketones under the same conditions give viscous solutions, which, in the case of methyl ethyl ketone after some time, deposits small crystals. Acetonitrile gives a colourless or very slightly coloured mass, probably

$$4MeCN,MgI_2,$$

which is decomposed by water without precipitation of magnesia. Butyronitrile gives a syrupy liquid which does not crystallise. Aluminium gives similar results, from acetone a brownish-yellow mass decomposed by water, and from acetonitrile several products, including a well crystallised, yellow substance, are obtained. E. H.

Action of a Solution of Zinc Hydroxide in Ammonia on Sugars. Adolf Windaus (*Ber.*, 1907, 40, 799—802).—In continuation of previous work on the formation of methylglyoxaline on dextrose (Abstr., 1905, i, 381; this vol., i, 90), the author has studied the behaviour of other sugars towards a solution of zinc hydroxide in ammonia. The various solutions examined were allowed to remain in a closed vessel at the ordinary temperature and in diffused daylight for four months. Working with *d*-mannose, *d*-fructose, *d*-sorbose, *l*-arabinose, and *l*-xylose, the author found methylglyoxaline in every case. With lactose, the yield of 4-methylglyoxaline was much less than with maltose or with dextrose. Methylglyoxaline was not obtained when sucrose was used.

Whilst in the cases quoted no other base, soluble in ether, was obtained in addition to methylglyoxaline, rhamnose formed a mixture of glyoxaline, 4-methylglyoxaline and 2 : 4-dimethylglyoxaline having been isolated, whilst acetaldehyde was also formed.

A peculiar intermediate product was obtained from *d*-galactose. When the latter remained in contact with an ammoniacal solution of zinc hydroxide for four days, crystals separated, which, when washed with 10% ammonia, were recrystallised from a mixture of alcohol and ammonia. The *compound*, $C_{12}H_{39}O_{16}N_3Zn$, obtained in this manner, softens at 70° and has m. p. about 77° (decomp.). When water is added to it, zinc hydroxide separates and the aqueous solution contains free ammonia. It reduces Fehling's solution. When boiled with nitric acid, it forms mucic acid; with phenylhydrazine acetate it yields galactosazone. The formula of a zinc galactosimine,

$$C_6H_{13}O_5N,C_6H_{16}O_5N_2,4H_2O,Zn(OH)_2,$$

is suggested. Methylglyoxaline may be obtained by heating the compound with ammonia for two hours at 100° under pressure.

Inosite does not form methylglyoxaline when acted on by an ammoniacal solution of zinc hydroxide. A complex *compound*, for which the formula $C_{12}H_{37}O_{18}N_3Zn_4$ is suggested, is formed, separating in needles. A. McK.

Cellulose Esters. Ernst Berl and Watson Smith, jun. (*Ber.*, 1907, **40**, 903—908).—Cellulose, according to Cross and Bevan, forms a tetra-acetate (calculated on $C_6H_{10}O_5$) and a trinitrate. The authors are in agreement with Ost, who states (Abstr., 1906, i, 560) that, at the most, only trisubstituted esters are formed.

Nitrated cellulose, saturated with glacial acetic acid, is treated with acetic anhydride and concentrated sulphuric acid; the white, powdery product contains more acetic acid and less nitrogen the greater the time occupied in its preparation, but a product free from nitrogen is obtained only under conditions in which the cellulose undergoes extensive degradation.

Reaction does not take place when the acetic anhydride in the preceding preparation is replaced by anhydrous formic acid; the latter, however, reacts with hydrocellulose to form a white powder which is hydrolysed by sodium hydroxide. Béhal's formic acetic anhydride converts hydrocellulose, in the presence of concentrated sulphuric acid, into yellowish-brown formyl compounds of degraded cellulose. C. S.

Ruthenium Halogen Salts. Alexander Gutbier and H. Zwicker (*Ber.*, 1907, **40**, 690—694).—The ruthenium halogen salts described were obtained either (1) by saturating the ruthenium halide solution with halogen and then mixing with a solution of the hydrochloride or hydriodide of the desired base, or (2) by mixing the ruthenium halide solution with the solution of haloid acid, dissolving any residue formed in dilute halogen acid and then passing chlorine or bromine into the cooled solution. The halogen salts which separate all crystallise well and are very stable and sparingly soluble. They undergo decomposition with water, but may, as a rule, be crystallised from aqueous solutions of the corresponding halogen acid. The chloro-salts are green, forming reddish-brown solutions with hydrochloric acid; the bromo-salts are bluish-black, forming dark blue solutions with hydrobromic acid.

Methylammonium ruthenichloride, $RuCl_6(NH_3Me)_2$, forms dark greenish-brown, hexagonal leaflets. *Methylammonium ruthenibromide*, $RuBr_6(NH_3Me)_2$, forms black, glistening leaflets. *Dimethylammonium ruthenichloride*, $RuCl_6(NH_2Me_2)_2$, forms glistening, dark green needles. *Dimethylammonium ruthenibromide*,

$$RuBr_6(NH_2Me_2)_2,$$

forms bluish-black, felted needles. *Trimethylammonium ruthenichloride*, $RuCl_6(NHMe_3)_2$, forms dark green needles. *Trimethylammonium ruthenibromide*, $RuBr_6(NHMe_3)_2$, forms bluish-black needles. *Ethylammonium ruthenichloride*, $RuCl_6(NH_3Et)_2$, forms glistening, green needles. *Ethylammonium ruthenibromide*,

$$RuBr_6(NH_3Et)_2,$$

forms bluish-black needles. *Diethylammonium ruthenichloride*, $RuCl_6(NH_2Et_2)_2$, forms glistening, brownish-green leaflets. *Diethylammonium ruthenibromide*, $RuBr_6(NH_2Et_2)_2$, was prepared. *Propylammonium ruthenichloride*, $RuCl_6(NH_3Pr)_2$, forms glistening, dark green needles. *Propylammonium ruthenibromide*, $RuBr_6(NH_3Pr)_2$, forms bluish-black, felted needles. *Dipropylammonium rutheni-*

chloride, $RuCl_6(NH_2Pr_2)_2$, forms dark green needles. iso*Butylammonium ruthenichloride*, $RuCl_6(C_4H_9 \cdot NH_3)_2$, forms glistening, dark green leaflets. iso*Butylammonium ruthenibromide*,

$$RuBr_6(C_4H_9 \cdot NH_3)_2,$$

forms glistening, bluish-black, felted needles. *Ethylenediammonium ruthenichloride*, $RuCl_6(C_2H_4N_2H_6)$, forms glistening, green needles. *Ethylenediammonium ruthenibromide*, $RuBr_6(C_2H_4N_2H_6)$, forms glistening, black needles. *Propylenediammonium ruthenichloride*,

$$RuCl_6(C_3H_6 \cdot N_2H_6),$$

forms greenish-black needles. *Propylenediammonium ruthenibromide*, $RuBr_6(C_3H_6N_2H_6)$, forms bluish-black needles. A. McK.

Stereoisomeric Hexammine Salts. ALFRED WERNER, F. BRÄUNLICH, E. ROGOWINA, and CHR. KREUTZER (*Annalen*, 1907, **351**, 65—86. Compare Abstr., 1900, i, 86).—Stereoisomerism has been observed with inorganic salts of the type $[M''A_2B_2]X$, when A_2 or B_2 is displaced by an acid group. In the present paper the preparation of stereoisomeric salts, in which this is not the case, is decribed. These compounds, $[Co\ en_2(NH_3)_2]X_3$ (En = ethylenediamine), are represented by space formulæ. The members of the *cis*-series, which are characterised by comparatively sparing solubility in water, are formed by the oxidation of dithiocyanodiethylenediaminecobalt salts with chlorine, whilst the *trans*-salts, which are readily soluble in water, are prepared by the action of concentrated ammonia on dinitratodiethylenediaminecobalt nitrate. The configuration of the salts is derived from the genetic relationship of the *cis*-series through the dithiocyanodiethylenediaminecobalt to the 1 : 2-dichlorodiethylenediaminecobalt salts of the "violeo" series.

Diethylenediamine-cis-*diamminecobalt Salts.*—The *chloride*,

$$[Co\ en_2(NH_3)_2]Cl,H_2O,$$

prepared by the action of chlorine on dithiocyanodiethylenediaminecobalt chloride in cold aqueous solution, crystallises in long, yellow, asymmetric prisms or thin needles, effloresces, and with nitric acid, hydrobromic acid, and potassium iodide in aqueous solution yields the corresponding *salts* as glistening, yellow, crystalline powders. Its aqueous solution forms crystalline precipitates also with potassium platinichloride, hydrogen platinichloride, auric chloride, mercuric chloride, and stannous chloride; the *bromide*, $[Co\ en_2(NH_3)_2]Br_3$, crystallises in long, flat prisms; the *iodide*, *nitrate*, *thiocyanate*, *dichromate*, and *mercurichloride*, $[Co\ en_2(NH_3)_2]Cl_3,5HgCl_2$, are described.

Diethylenediamine-trans-*diamminecobalt Salts.*—When heated on the water-bath with nitric acid, D 1·4, 1 : 2-dinitritodiethylenediaminecobalt nitrate is converted into *dinitratodiethylenediaminecobalt nitrate*, $[Co\ en_2(NO_3)_2]NO_3$, which is obtained in dark red, triclinic crystals, and reacts with liquid ammonia or ammonia in concentrated aqueous solution, forming *diethylenediamine*-trans-*diamminecobalt nitrate* together with a small amount of the *cis*-salt. The *trans*-nitrate is obtained as a red, viscid syrup, which is soluble in water, and on addition of potassium iodide yields the *iodide*, $[Co\ en_2(NH_3)_2]I_3$; this separates from hot water in small, orange-yellow crystals or strongly refracting, rhombic plates.

The *bromide*, $[\mathrm{Co\ en_2(NH_3)_2}]\mathrm{Br_3}$; *cobaltochloride*, $[\mathrm{Co\ en_2(NH_3)_2}]\mathrm{Cl_3,CoCl_2}$; *platinichloride*, $[\mathrm{Co\ en_2(NH_3)_2}]_2\mathrm{3PtCl_6,12H_2O}$, and *aurichloride*, which is a mixture of $[\mathrm{Co\ en_2(NH_3)_2}]\mathrm{Cl,2AuCl_4}$ and $[\mathrm{Co\ en_2(NH_3)_2}]\mathrm{Cl_2,AuCl_4}$, are prepared from the iodide by the successive action of silver oxide or nitrate and hydrobromic acid or metallic chloride. G. Y.

Structurally Isomeric Thiocyanates and Nitrites. ALFRED WERNER (*Ber.*, 1907, **40**, 765—788).—This research is a contribution to the isomerism of inorganic compounds ("Salzisomerie"). Basing his experiments on the fact that thiocyanic acid forms two series of isomeric compounds of the types $\mathrm{N\vdots C\cdot S\cdot C_nH_{2n+1}}$ and $\mathrm{S\vdots C\vdots N\cdot C_nH_{2n+1}}$, the author had previously shown, conjointly with Bräunlich (Abstr., 1900, i, 86), that two isomeric dithiocyanodiethylenediaminecolbaltisalts of the types $[\mathrm{(SCN)_2Co\ en_2}]\mathrm{X}$ and $[\mathrm{(NCS)_2Co\ en_2}]\mathrm{X}$ exist; the structural difference between them is shown by their behaviour on oxidation. In continuation of the work of Werner and Klien (*loc. cit.*) on thiocyanonitrotetramminecobalt salts of the type

$$\left[\begin{matrix}\mathrm{NCS}\\ \mathrm{O_2N}\end{matrix}\mathrm{Co(NH_3)_4}\right]\mathrm{SCN},$$

the corresponding *iso*thiocyano- [thiocarbimide]-compounds are now described, so that the following *iso*thiocyano-types are now known in the cobalt series: $\left[\mathrm{NCSCo(NH_3)_5}\right]\mathrm{X_2}$, $\left[\begin{matrix}\mathrm{SCN}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co(NH_3)_4}\right]\mathrm{X_2}$, $\left[\begin{matrix}\mathrm{SCN}\\ \mathrm{O_2N}\end{matrix}\mathrm{Co(NH_3)_4}\right]\mathrm{X}$, $\left[\mathrm{(SCN)_2Co\ en_2}\right]\mathrm{X}$, and $\left[\mathrm{(SCN)_2Co\ pn_2}\right]\mathrm{X}$, whilst the following thiocyano-types are known: $\left[\begin{matrix}\mathrm{NCS}\\ \mathrm{Cl}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{X}$, $\left[\begin{matrix}\mathrm{O_2N}\\ \mathrm{NCS}\end{matrix}\mathrm{Co(NH_3)_4}\right]\mathrm{X}$, and $\left[\mathrm{(NCS)_2Co\ en_2}\right]\mathrm{X}$.

Since nitrous acid forms isomeric nitrites and nitro-compounds, isomeric compounds of the types $[\mathrm{NO_2Co(NH_3)_5}](\mathrm{NO_2})_2$ and $[\mathrm{NO\cdot O\cdot Co(NH_3)_5}](\mathrm{NO_2})_2$ had previously been described by Jörgensen; the latter *iso*xantho-compound, however, had been somewhat imperfectly examined on account of its instability and its slight solubility. The author now places beyond doubt the fact that isomeric compounds of the types in question exist.

Ammonium thiocyanate was fused and cobalt oxide gradually added. After the addition, first of ammonia and then of water, the resulting red solution was decomposed with concentrated hydrochloric acid and the crude chloride acted on by dilute sulphuric acid, when iso*thiocyanopentamminecobaltisulphate*, $[\mathrm{NCSCo(NH_3)_5}]\mathrm{SO_4,2H_2O}$, separates; it crystallises from dilute acetic acid in glistening, yellowish-red leaflets, which, when dehydrated, are transformed into a yellow powder. The *nitrate* was also prepared. When the sulphate is oxidised by chlorine, it is converted into hexammine-cobalt chloride.

For the preparation of salts of the type $[\mathrm{SCNCo(H_2O)(NH_3)_4}]\mathrm{X_2}$, a mixture of ammonium thiocyanate and diaquotetramminecobalt sulphate, $[(H_2O)_2Co(NH_3)_4]_2(SO_4)_3,3H_2O$, is heated with dilute acetic acid and potassium bromide added to the filtrate. Since the bromide could not be obtained pure, the crude product was acted on by concentrated hydrochloric acid, when *isothiocyanoaquotetramminecobalt chloride*, $[SCNCo(H_2O)(NH_3)_4]Cl_2$, separates as a brick-red precipitate; its aqueous solution is red, and, when acted on by chlorine, forms chloropentamminecobalt chloride according to the equation

$$[SCNCo(H_2O)(NH_3)_4]Cl_2 + 4Cl_2 + 5H_2O = [H_3NCoCl(NH_3)_4]Cl_2 + H_2SO_4 + CO_2 + 7HCl.$$

The *nitrate* forms dark red, glistening crystals. The *nitrite* is a dark brownish-red, crystalline powder, and, for the preparation of salts of the type $[O_2NCo(SCN)(NH_3)_4]X$, is converted by heating at 70—80° into *iso*thiocyanonitrotetrammin-cobalt nitrite, thus,

$$[SCNCo(H_2O)(NH_3)_4](NO_2)_2 = H_2O + [O_2NCo(SCN)(NH_3)_4]NO_2.$$

By the addition of potassium bromide to the latter compound, *isothiocyanonitrotetramminecobaltibromide*, $[O_2NCo(SCN)(NH_3)_4]Br,H_2O$, is formed; it crystallises in yellowish-brown needles. When oxidised by chlorine, it forms nitropentamminecobaltichloride, thus:

$$[O_2NCo(SCN)(NH_3)_4]Cl + 4Cl_2 + 6H_2O = [O_2NCo(NH_3)_5]Cl_2 + H_2SO_4 + CO_2 + 7HCl.$$

The *nitrate*, $[O_2NCo(SCN)(NH_3)_4]NO_3,H_2O$, is a flesh-coloured, microcrystalline powder. The *iodide* forms a dark flesh-coloured microcrystalline aggregate.

Chlorothiocyanodiethylenediaminecobalt thiocyanate,

$$[NCSCoCl\ en_2]SCN,$$

obtained from potassium thiocyanate and dichlorodiethylenediaminecobalt chloride, forms reddish-violet crystals. The *iodide* forms glistening, reddish-violet leaflets. The *dichromate* forms chocolate-coloured leaflets.

1 : 2-*Dinitritodiethylenediaminecobaltibromide*,

$$\left[\begin{matrix}(1)\ ON{\cdot}O \\ (2)\ ON{\cdot}O\end{matrix}Co\ en_2\right]Br,$$

prepared by the addition of sodium nitrite to an aqueous solution of 1 : 2-diaquodiethylenediaminecobaltibromide containing a little acetic acid, is sparingly soluble in water, forming a brownish-orange solution, which, when heated, becomes yellow. After several hours at the ordinary temperature, the brownish-red tint of the dry salt becomes a yellowish-brown, owing to the formation of 1 : 2-dinitrodiethylenediaminecobalt bromide, $\left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}Co\ en_2\right]Br$. The transformation is complete when the nitrito-compound is heated at 80° for two hours. The two isomerides differ in their behaviour towards ammonium sulphate. Whilst the addition of ammonium sulphate to a solution of the nitro-bromide causes an immediate precipitation of the sparingly soluble flavo-sulphate, no precipitate is obtained with the nitrito-bromide. The nitrito-compound evolves nitrous fumes when acidified by hydrochloric acid.

The corresponding *nitrate* forms reddish-brown crystals and is readily converted into the isomeric nitro-compound on remaining at the ordinary temperature. The *iodide* forms a microcrystalline, chocolate-coloured powder and, on remaining at the ordinary temperature, is converted into the chamois-brown isomeride. The *dithionate* forms glistening, silky, brown needles and on remaining at the ordinary temperature is converted into the brownish-yellow isomeride.

1 : 6-*Dinitritodiethylenediaminecobaltichloride*,

$$\left[\begin{matrix}(1)\ \mathrm{ON{\cdot}O}\\(6)\ \mathrm{ON{\cdot}O}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Cl},$$

obtained by the action of sodium nitrite on 1 : 6-diaquodiethylenediaminecobaltichloride, forms yellowish-red crystals, which evolve nitrous fumes when acidified by mineral acids. With hydrochloric acid, it forms 1 : 6-diaquodiethylenediaminecobalt chloride. After forty-eight hours at the ordinary temperature, the salt is transformed into the isomeric croceo-chloride, $\left[\begin{matrix}(1)\ \mathrm{O_2N}\\(6)\ \mathrm{O_2N}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Cl}$, which is only slowly attacked by cold hydrochloric acid and with warm hydrochloric acid is converted into 1 : 6-chloronitrodiethylenediaminecobalt chloride.

The corresponding *bromide* contains $1H_2O$ and forms yellowish-red needles, which, after some hours at the ordinary temperature or more quickly at 60°, are converted into the yellow nitro-compound. The isomerides differ in their behaviour towards hydrochloric acid, the former yielding 1 : 6-diaquodiethylenediaminecobalt chloride and nitrous acid, whilst the latter, when warmed with concentrated hydrochloric acid, gives the red coloration characteristic of croceo-salts, and forms 1 : 6-chloronitrodiethylenediaminecobalt chloride, thus: $[(\mathrm{O_2N})_2\mathrm{Co\ en_2}]\mathrm{Br} + 2\mathrm{HCl} = [\mathrm{O_2NCoCl\ en_2}]\mathrm{Cl} + \mathrm{HNO_2} + \mathrm{HBr}$.

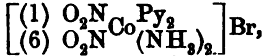
The *iodide* forms brownish-red needles which are readily transformed into the yellow isomeride. The *nitrate* forms dark brownish-red crystals, and at 110° is readily converted into the croceo-salt. The *dithionate* forms brick-red needles. The *thiocyanate* forms glistening, reddish-yellow crystals, which are very readily transformed into a yellow powder.

1 : 6-*Dinitritodipyridinediamminecobaltibromide*,

$$\left[\begin{matrix}(1)\ \mathrm{ON{\cdot}O}\\(6)\ \mathrm{ON{\cdot}O}\end{matrix}\mathrm{Co}\begin{matrix}\mathrm{Py_2}\\(\mathrm{NH_3})_2\end{matrix}\right]\mathrm{Br,H_2O},$$

obtained by the action of sodium nitrite on an aqueous solution of hydroxoaquodipyridinediamminecobalt chloride containing the requisite amount of acetic acid, forms glistening, copper-coloured leaflets. Nitrous acid is evolved by the action of hydrochloric acid. The *iodide* forms glistening, copper-coloured leaflets and, after some weeks at the ordinary temperature, is transformed into the yellow isomeride. The *nitrate* forms bronze-coloured leaflets and may be kept for weeks at the ordinary temperature without undergoing change. After six weeks, however, the transformation into the yellowish-orange isomeride is complete. The *dithionate* contains $4H_2O$ and forms glistening, yellowish-red crystals and, after some weeks at the ordinary temperature, is converted into the yellow isomeride. The *thiocyanate* forms silvery, reddish leaflets and appears to be the most stable of the dinitrito-compounds studied, since no alteration of its tint was detected.

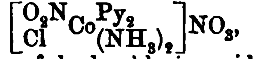
1 : 6-*Dinitrodipyridinediamminecobaltibromide*,



$$\left[\begin{matrix}(1)\ O_2N & & Py_2\\ & Co & \\ (6)\ O_2N & & (NH_3)_2\end{matrix}\right]Br,$$

prepared by heating the preceding dinitrito-compound at 60°, separates from dilute acetic acid in yellow needles and is more sparingly soluble in water than the dinitrito-compound. The *nitrate* crystallises from water in brownish-yellow prisms. The *dithionate* contains $2H_2O$ and is a yellow powder.

Chloronitrodipyridinediamminecobalt nitrate,



$$\left[\begin{matrix}O_2N & & Py_2\\ & Co & \\ Cl & & (NH_3)_2\end{matrix}\right]NO_3,$$

obtained by the action of hydrochloric acid on dinitrodipyridinediamminecobalt bromide, forms a bluish-red, crystalline powder.

A. McK.

Di*iso*thiocyanodipropylenediamine- and Dipropylenediamine-diammine-cobalti-salts. ALFRED WERNER and K. DAWE (*Ber.*, 1907, **40**, 789—799. Compare preceding abstract).—The *iso*thiocyano-compounds described were obtained by heating potassium thiocyanate with 1 : 6-dichlorodipropylenediaminecobalt chloride, thus:

$$[Cl_2Co\ pn_2]Cl + 3KSCN = [(SCN)_2Co\ pn_2]SCN + 3KCl\ [pn = C_3H_6(NH_2)_2].$$

The product of this action is homogeneous and, from its behaviour on oxidation with chlorine, is di*iso*thiocyanodipropylenediaminecobalt thiocyanate. This result is contrasted with the formation of two isomerides, thiocyano- and *iso*thiocyano-compounds, as products of the action of potassium thiocyanate on dichlorodiethylenediaminecobalt chloride.

If a current of chlorine be passed into solutions of the *iso*thiocyano-salts described, oxidation occurs with the formation of dipropylene diaminediamminecobalti-salts of the type $[(H_3N)_2Co\,pn_2]X_3$, a proof that the compounds in question are *iso*thiocyano-salts.

Diïsothiocyanodipropylenediaminecobaltithiocyanate,

$$[(SCN)Co\ pn_2]SCN,H_2O,$$

forms tetragonal prisms. The *chloride* forms red, hexagonal prisms and contains $1H_2O$. The *bromide* has $1\frac{1}{2}H_2O$ and separates from water in rhombic prisms; it effloresces on exposure to air. The *iodide* has $1\frac{1}{2}H_2O$ and forms brownish-red crystals. The *antimony tetrachloride* compound, $[(SCN)_2Co\ pn_2]SbCl_4$, separates in blood-red, glistening, spear-shaped crystals.

Dipropylenediaminediamminecobaltichloride, $[(H_3N)_2Co\ pn_2]Cl_3,H_2O$, separates from water in golden-yellow, hexagonal prisms. The *bromide*, prepared by the addition of hydrobromic acid to the chloride, has $1H_2O$ and separates in golden-yellow needles. When potassium iodide is added to an aqueous solution of the chloride, two isomeric *iodides*, $[(H_3N)_2Co\ pn_2]I_3,H_2O$, are formed; the more sparingly soluble of the two forms dark orange-red, brittle crystals, whilst the crop, which separates from the mother liquor, crystallises in needles of a yellower tint than that of the isomeride. No other isomerides in this series have been observed. The *nitrate* forms straw-yellow leaflets. The *dichromate* forms reddish-yellow needles. The *dithionate* crystallises in orange-coloured leaflets. The *cobalt chloride* compound, $[(H_3N)_2Co\ pn_2]Cl_3,CoCl_2,2H_2O$, forms bright green leaflets or scales, sometimes stellate crystals and prismatic needles. The *stannous chloride* compound, $[(H_3N)_2Co\ pn_2]Cl_3,2SnCl_2$, forms glistening, yellowish-red crystals. The *mercurous chloride* compound,

$$[(H_3N)_2Co\ pn_2]Cl_3,2HgCl_2,$$

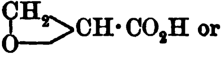
forms iridescent needles or prisms. The *aurichloride*,

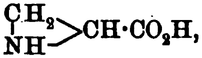
$$[(H_3N)_2Co\ pn_2]Cl_3,AuCl_3,$$

forms golden-yellow needles. A. McK.

Two New Methods of Formation of *iso*Serine.

CARL NEUBERG and PAUL MAYER (*Biochem. Zeitsch.*, 1907, **3**, 116—120. Compare Abstr., 1904, i, 220, 230; 1906, i, 937).—*iso*Serine is formed by the action of a 50% solution of hydrogen cyanide on a solution of aminoacetaldehyde hydrochloride (Fischer, Abstr., 1893, i, 187, 300) made alkaline with ammonium hydroxide.

The same product may be obtained by the action of ammonia and ammonium carbonate on α-bromo-β-hydroxypropionic acid (Beckurts and Otto, Abstr., 1885, 506) at 100° under pressure. The formation of *iso*serine (β-amino-α-hydroxypropionic acid) and not serine (α-amino-β-hydroxypropionic acid) is probably due to the intermediate formation of a cyclic compound, for example,  $\begin{matrix}CH_2\\ |\\ O\end{matrix}\!\!>CH\cdot CO_2H$ or



$$\begin{matrix}CH_2\\ |\\ NH\end{matrix}\!\!>CH\cdot CO_2H,$$

and the subsequent addition of ammonia or water. J. J. S.

Synthesis of Polypeptides. XVI. Derivatives of *d*-Alanine.

EMIL FISCHER and ARNOLD SCHULZE (*Ber.*, 1907, **40**, 943—954).—Glycyl-*d*-alanine has been synthesised in order to determine whether it is identical with one of the hydrolytic products of silk fibroin (Fischer and Abderhalden, Abstr., 1906, i, 326). The synthetical product yields an anhydride which is identical with the anhydro-compound from silk.

Chloroacetyl-d-*alanine*, $C_5H_8O_3NCl$, obtained by the action of chloroacetyl chloride on *d*-alanine in the presence of *N*-sodium hydroxide solution at low temperatures, separates from ethyl acetate in large colourless plates, m. p. 93·5—94·5° (corr.). With ammonia it yields *glycyl*-d-*alanine*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, which crystallises from a mixture of alcohol and water in long needles, m. p. about 233° (decomp.) after changing colour at 218°; $[\alpha]_D^{20}$ $-50°$. It is completely hydrolysed when heated in a sealed tube in a boiling water-bath for seven hours with 10% hydrochloric acid. When converted into the hydrochloride of its ester and then poured into strongly cooled alcoholic ammonia, which was saturated at 0°, it yields the anhydride (Fischer and Abderhalden, *loc. cit.*). This has $[\alpha]_D^{20}$ $-5·0°$, and is more readily prepared by the action of ammonia on the ethyl ester of chloroacetyl-*d*-alanine.

d-α-Bromopropionic acid, obtained by the action of bromine and nitric oxide on *d*-alanine, has $[\alpha]_D$ $+40·28°$. The chloride of the acid condenses with *d*-alanine in the presence of sodium hydroxide, yielding d-*bromopropionyl*-d-*alanine*, $C_6H_{10}O_3NBr$, which crystallises from water or alcohol in well-developed octahedral crystals, m. p. 175° (corr.) (decomp.), $[\alpha]_D^{21}$ $-16·5°$. The corresponding compound obtained from inactive α-bromopropionic acid, dl-α-*bromopropionyl*-d-*alanine*, is somewhat sparingly soluble in water, but readily in methyl alcohol. It has no definite m. p.; when heated quickly, it begins to sinter at 170° (corr.) and melts and decomposes at 173—174°. The methyl-alcoholic solution has $[\alpha]_D^{20}$ $-26·5$ and the aqueous solution $[\alpha]_D^{23}$ $-42·4$. It is impossible to separate the two components, namely, *d*-bromopropionyl-*d*-alanine and *l*-bromopropionyl-*d*-alanine, which appear to be present in equal amounts. The product, however, is not necessarily a definite compound of the two. *d*-Alanyl-*d*-alanine can be readily isolated from the product obtained by the action of ammonia on the mixed bromo-derivatives.

A discussion on the meaning of the expression "partially racemic" is contained in the paper. J. J. S.

Influence of Temperature and Concentration on the Rotatory Power of Aqueous Solutions of Certain Alkyl Hydrogen Aspartates. ARNALDO PIUTTI and GENNARO MAGLI (*Gazzetta*, 1906, **36**, ii, 738—781).—The alkyl hydrogen aspartates examined by the authors were the methyl, ethyl, allyl, propyl, *iso*propyl, butyl, *iso*butyl, and amyl esters, which have been prepared by F. Mastrangioli and E. Stanzani, who also carried out some of the polarimetric measurements described below. A description of the above esters is followed by curves and tables giving the rotatory powers at different temperatures of aqueous solutions of 0·4, 0·2, and 0·1-molar concentrations. The rotatory powers of the sodium salts of these esters were also determined in solutions of 0·2-molar concentration at temperatures lying between 10° and 90°.

Methyl hydrogen aspartate, $CO_2H·CH(NH_2)·CH_2·CO_2Me$, separates in shining, white plates, m. p. 180—181° (decomp.), and dissolves in water or alcohol. Its *copper* salt, $(C_5H_8O_4N)_2Cu$, crystallises from water in nacreous, blue plates.

Ethyl hydrogen aspartate, $CO_2H·CH(NH_2)·CH_2·CO_2Et$, crystallises from alcohol in thin, shining plates and from water in thick plates, m. p. 189—190°, decomposing at 192°. The *copper* salt,

$$(C_6H_{10}O_4N)_2Cu,$$

crystallises in laminæ.

Allyl hydrogen aspartate, $CO_2H·CH(NH_2)·CH_2·CO_2·C_3H_5$, forms yellow, acicular crystals, m. p. 194—195°, and dissolves in water. Its *copper* derivative, $(C_7H_{10}O_4N)_2Cu$, crystallises in blue plates.

Propyl hydrogen aspartate, $CO_2H·CH(NH_2)·CH_2·CO_2Pr^{\alpha}$, forms nacreous, white scales, m. p. 200°, and dissolves readily in water and sparingly in alcohol. The *copper* salt, $(C_7H_{12}O_4N)_2Cu$, was prepared and analysed.

iso*Propyl hydrogen aspartate*, $CO_2H·CH(NH_2)·CH_2·CO_2Pr^{\beta}$, crystallises from water in long, white needles, m. p. 209—210°, and is slightly soluble in water. The *copper* derivative, $(C_7H_{12}O_4N)_2Cu$, was prepared and analysed.

Butyl hydrogen aspartate, $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2{\cdot}C_4H_9$, forms pearly, white scales, m. p. 197—198°, and dissolves readily in water and sparingly in alcohol. The *copper* salt, $(C_8H_{14}O_4N)_2Cu$, crystallises in blue plates.

iso*Butyl hydrogen aspartate*, $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2{\cdot}C_4H_9$, forms white scales, m. p. 197—198°, and is readily soluble in water and slightly so in alcohol. The *copper* derivative, $(C_8H_{14}O_4N)_2Cu$, was prepared and analysed.

iso*Amyl hydrogen aspartate*, $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2{\cdot}C_5H_{11}$, crystallises in nacreous, white plates, m. p. 195—196°, and dissolves readily in water and sparingly in alcohol. The *copper* salt,

$$(C_9H_{16}O_4N)_2Cu,$$

was prepared and analysed.

All these alkyl hydrogen aspartates are dextrorotatory at the ordinary temperature, but lævorotatory at high temperatures. The following table gives the temperatures at which the aqueous solutions of the three concentrations examined become inactive:

		Temperature of inactivity.		
	Mol. Wt.	0·4 Molar.	0·2 Molar.	0·1 Molar.
Methyl hydrogen aspartate	147	45·2°	35·5°	43·7°
Ethyl ,, ,,	161	63·3°	49·5°	63°
Allyl ,, ,,	173	67·8°	46°	40·5°
Propyl ,, ,,	175	75·1°	73°	64°
*iso*Propyl ,, ,,	175	87·3°	83°	59°
Butyl ,, ,,	189	74°	76°	78·7°
*iso*Butyl ,, ,,	189	81·7°	79·5°	73°
*iso*Amyl ,, ,,	303	[77°]	91°	80·3°

The results show that the rotatory powers of the alkyl hydrogen aspartates in aqueous solutions are directly proportional to the molecular weight and to the concentration of the solution. The authors regard the change of sign of the optical activity of solutions of these esters to be due to their gradual electrolytic dissociation as the temperature is raised, the free anions being lævorotatory.

The rotatory powers of the sodium salts of these esters are negative between 10° and 90°, except in the case of sodium *iso*propyl aspartate, which is dextrorotatory below about 22° and lævorotatory above that temperature. As these sodium compounds are undoubtedly more highly dissociated in aqueous solution than the alkyl hydrogen esters themselves, support is lent to the view that the change in sign of the rotation is due to dissociation. T. H. P.

New Method of Preparing Amides of Substituted Malonic and Acetoacetic Acids. HANS MEYER (*Monatsh.*, 1907, 28, 1—5. Compare Abstr., 1906, i, 137, 358; this vol., i, 179).—Hitherto, ethylmalonamides have been prepared by way of the acid chlorides, whilst of disubstituted acetoacetamides only the dimethyl and methylethyl derivatives are formed by the action of aqueous ammonia on the esters. The author has found that monosubstituted acetoacetamides, which are formed readily by the action of ammonia on the esters, can be alkylated by boiling with the sodium alkyloxide and alkyl iodide. Ethylmalonamide also can be prepared in this manner in good yields from malonamide.

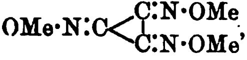
Diethylacetoacetamide, $C_8H_{15}O_2N$, prepared in an 80% yield from ethylacetoacetamide, crystallises in long needles, m. p. 122—123°.

Methylpropylacetoacetamide, $C_8H_{15}O_2N$, m. p. 125°, obtained in a 70% yield from methylacetoacetamide, crystallises from water.

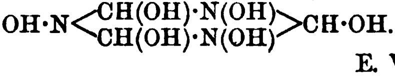
Ammonia reacts more easily with methyl- than with ethyl-acetoacetate; with sodium methoxide and methyl iodide, the resulting acetoacetamide forms methyl- or, with an excess of the reagents, dimethyl-acetoacetamide. G. Y.

Derivatives of Fulminic Acid. F. CARLO PALAZZO and A. TAMBURELLO (*Chem. Zentr.*, 1907, i, 26—27; from *Estr. Giorn. Sci. Nat. Econ.*, 26).—Determination of the molecular weight of metafulminic or *iso*cyanuric acid, prepared by Scholvien's method (Abstr., 1885, 39; 1886, 137) and dehydrated in a vacuum over sulphuric acid, by Raoult's freezing-point method using glacial acetic acid, gave 129·5, and correspond therefore with the formula $(CNOH)_3$. 0·5—1 Gram of the acid is completely dehydrated in a day, and the acid also loses water on exposure to the air. The anhydrous acid explodes at 106°. The anhydrous and the hydrated acids have the same formula, since both yield the same *ester*, $C_3N_3(OMe)_3$, when treated with a solution of diazomethane in ether at $-10°$. The ester, b. p. 126°/18 mm., is an almost colourless liquid and is insoluble in water or alkalis; the molecular weight determined by the freezing-point method, using glacial acetic acid, was found to be 160·7. When the hydrate of metafulminic acid is boiled with dilute sulphuric acid in a reflux apparatus for an hour, hydrocyanic and oxalic acids can be detected in the distillate, whilst the residue contains ammonia and hydroxylamine; carbon dioxide is also liberated. Hydrochloric acid acts in the same way, but less hydrocyanic acid is formed; when metafulminic acid is heated, however, with either acid at 130—140°, hydrocyanic acid is not formed, but carbon dioxide is evolved. The behaviour of metafulminic acid shows, therefore, that it contains three unchanged oximide groups, and an aqueous solution of sodium fulminate gives the characteristic coloration of hydroxamic acids with ferric chloride.

By the action of methyl sulphate on sodium fulminate the *ester*,



$OMe{\cdot}N{:}C{<}\begin{matrix}C{:}N{\cdot}OMe\\ |\\ C{:}N{\cdot}OMe\end{matrix}$, m. p. 149°, is obtained; it forms slender, white needles. By the action of benzoyl chloride on the fulminate a *compound*, m. p. 138°, is formed. The formula of the hydrate of metafulminic acid is probably



$OH{\cdot}N{<}\begin{matrix}CH(OH){\cdot}N(OH)\\ CH(OH){\cdot}N(OH)\end{matrix}{>}CH{\cdot}OH$.

E. W. W.

Cyanuric Derivatives. HERMANN FINGER (*J. pr. Chem.*, 1907, [ii], 75, 103—104).—A preliminary communication.

Cyanuric trihydrazide, $C_3N_3(NH{\cdot}NH_2)_3$, is obtained by acting on cyanuric chloride dissolved in cyanomethane with hydrazine hydrate;

it reacts with aldehydes, isatin and ethyl acetoacetate, forming condensation products; its hydrochloride is converted by sodium nitrite into a substance which explodes on heating and is converted by sodium hydroxide into what is probably *cyanuric triazide*, C_3N_{12}. Cyanuric chloride dissolved in acetone reacts with silver nitrate with the probable formation of *trinitrocyanidine*, $C_3N_3(NO_2)_3$. W. H. G.

Cyanogen, Hydrogen Cyanide, and Acetylene Equilibria. H. von Wartenberg (*Zeit. anorg. Chem.*, 1907, **52**, 299—315. Compare Wallis, Abstr., 1906, i, 730).—The experiments have been made chiefly with the object of testing Nernst's equations connecting chemical equilibrium and temperature.

It has been calculated that nitrogen at atmospheric pressure and carbon should be in equilibrium with 44% of cyanogen at 3500°, but, although the spectrum of the latter gas is very prominent in the electric arc, the author finds, in agreement with Wallis (*loc. cit.*), that no cyanogen, but only hydrogen cyanide, can be detected in the gases drawn from the arc chamber. This result may be due partly to the carbon particles in the flame exerting a catalytic action on the decomposition of cyanogen and partly to combination of the latter with hydrogen, which cannot readily be removed from graphite.

The equilibrium in the reaction $2C + H_2 + N_2 = 2HCN$,—59,700 cal., has been investigated by passing a dry mixture of equal volumes of the gases over a glowing carbon rod in a special apparatus and analysing the resulting gases. At 1875°, 1752°, and 1635°, the equilibrium concentration of hydrogen cyanide amounts to 4·7, 3·1, and 1·95% respectively, in satisfactory agreement with Nernst's formula.

Corresponding experiments on the formation of acetylene from hydrogen and carbon were carried out in the same apparatus, but as very high temperatures could not be used owing to destruction of the carbon rods, and the reaction is very slow at lower temperatures, the results are only of a preliminary nature. At 1824° the corrected value gives 0·13% of acetylene, whilst Nernst's equation, allowing for the difference of the specific heats of acetylene and hydrogen, gives a considerably higher value; the discrepancy may be due to decomposition of the acetylene as the temperature falls.

The work of Pring and Hutton (Trans., 1906, **89**, 1591) on this subject is criticised. G. S.

Preparation of Alkali Cyanides. O. Schmidt (D.R.-P. 176080).—The nitrides of calcium and magnesium and other allied metals, when heated to redness with carbon and an alkali carbonate, are readily transformed into alkali cyanides. The access of air must be avoided; the reaction when started is exothermic and the best results are obtained when the proportions correspond with the following equation: $Mg_3N_2 + Na_2CO_3 + C = 2NaCN + 3MgO$,

It is, however, unnecessary to isolate the nitride; the formation of cyanide takes place in one operation when nitrogen is passed over a mixture of magnesium, sodium carbonate, and carbon heated to redness, and the absorption of the nitrogen is very rapid:

$$3Mg + N_2 + Na_2CO_3 + C = 2NaCN + 3MgO.$$

G. T. M.

Alkylation of the Metallic Cyanides. H. GUILLEMARD (*Compt. rend.*, 1907, **144**, 326—328).—The author has studied the effect of temperature and duration of reaction on the proportions of nitrile and carbylamine obtained by the action of alkylating agents on various metallic cyanides. The quantities of the two isomerides in the reaction product were estimated by the method previously described (this vol., ii, 141). The general conclusion drawn is that the cyanides on alkylation at a low temperature give carbylamines, at a higher temperature a mixture of carbylamine and nitrile, and above a certain temperature nitrile only. This supports Nef's hypothesis that the cyanides correspond with the formula MNC, at least at low temperatures. The formation of nitriles at higher temperatures can be explained by various hypotheses. (1) By an alteration in the constitution of the cyanides at high temperatures; (2) by a variation in the method of reaction of the cyanide (of fixed constitution) at high temperatures; (3) by isomeric change at high temperature of the carbylamine formed at low temperature into nitrile. The evidence is mostly in support of the last theory, the author having shown previously (this vol., i, 197) that the carbylamines, on dissociating from their compounds with the cyanides, easily change into nitriles. E. H.

Allyl Cyanide and Allylthiocarbimide. CÆSAR POMERANZ (*Annalen*, 1907, **351**, 354—362).—This work was undertaken to throw light on the mechanism of the reaction by which allyl cyanide, the constitution of which as crotononitrile has been established by Lippmann (Abstr., 1892, 27) and Schindler (*ibid.*, 32) is formed from allyl haloids.

In the absence of water, allyl bromide does not react with potassium cyanide in a sealed tube at 120°, but a good yield of the nitrile is obtained if a small amount of water is present. This together with the observation that propylene dicyanide, which is formed from allyl chloride and potassium cyanide in dilute alcoholic solution (Pinner, Abstr., 1880, 99), yields potassium cyanide when shaken with aqueous potassium hydroxide, points to the formation of crotononitrile taking place in three stages: $KCN + H_2O = KOH + HCN$;

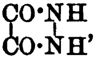
$$CH_2{:}CH{\cdot}CH_2Br + KCN + HCN = CN{\cdot}CHMe{\cdot}CH_2{\cdot}CN + KBr;$$

$CN{\cdot}CHMe{\cdot}CH_2{\cdot}CN + KOH = CHMe{:}CH{\cdot}CN + KCN + H_2O$. The water being reformed acts as a catalyst. The hydrolysis of crotononitrile with 25% sulphuric acid leads to the formation of *iso*crotonic acid.

As natural mustard oil contains allyl cyanide, and according to Will and Körner this substance is formed by the action of water on the oil (*Annalen*, 1863, **125**, 273), it seemed probable that the synthetical thiocarbimide might be a mixture of the allyl and propenyl compounds. On oxidation with sodium dichromate and sulphuric acid, it yields formic acid and small amounts of acetic acid which can be formed only from the propenylthiocarbimide. As propenyl compounds boil at higher temperatures than the corresponding allyl derivatives, it is probable that most of the propenyl thiocarbimide formed in the preparation of allylthiocarbimide, is removed in the fractions of higher boiling point.

G. Y.

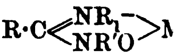
Ethyl Oxalylbishydrazoneacetoacetate. Decomposition Products of Esters of β-Ketonic Acid Acylhydrazones. CARL BÜLOW and MARTIN LOBECK (*Ber.*, 1907, 40, 708—719).—*Ethyl oxalylbishydrazoneacetoacetate*, $C_2O_2(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)_2$, m. p. 133·5°, obtained from oxalylhydrazide and ethyl acetoacetate in 89% yield, forms colourless needles, and reduces silver, gold, and copper salts. When heated at 187°, it decomposes into alcohol, ethyl acetoacetate, a *substance*, $C_8H_8O_2N_2$, m. p. 247°, and a *substance*, m. p. >290°, which is insoluble in alcohol. The former is identical with the compound obtained by Rosengarten (Abstr., 1894, i, 546) from hydrazine and ethyl acetylacetoacetate, and is also obtained from 3-methylpyrazolone and ethyl acetoacetate at 150°. The substance, m. p. >290°, is probably *cyclo*oxalylhydrazide,



$\begin{matrix}CO\cdot NH\\ | \quad\ \ |\\ CO\cdot NH\end{matrix}$, since the only products of hydrolysis are hydrazine and oxalic acid. The following reagents decompose ethyl oxalylbishydrazoneacetoacetate: boiling water yields ethyl acetoacetate and oxalylhydrazide; boiling 6% sodium acetate yields ethyl acetoacetate, oxalic acid, hydrazine, and 3-methylpyrazolone, thus disproving Curtius's statement that ethyl acetoacetate-acylhydrazones cannot be transformed into pyrazolone derivatives (Abstr., 1895, i, 32); phenylhydrazine yields oxalylhydrazide and phenylmethylpyrazolone; potassium hydroxide yields methylpyrazolone; boiling acetic anhydride yields *diacetyloxalylhydrazide*, $C_6H_{10}O_4N_4,2H_2O$, m. p. 273° (decomp.); boiling dilute sulphuric acid causes profound decomposition and hydrazine sulphate is isolated; benzaldehyde and boiling water yield dibenzaldehydeoxalyldihydrazone; concentrated sulphuric acid and resorcinol produce β-methylumbelliferone and oxalylhydrazide.

C. S.

Abnormal Metallic Salts of Hydroxyamidines and Allied Compounds. Theory of Internally Complex Metallic Salts. HEINRICH LEY and P. KRAFFT (*Ber.*, 1907, 40, 697—707. Compare Abstr., 1901, i, 759; 1902, i, 445; 1903, i, 282).—In attempting to account for the abnormal colour of the copper, nickel and cobalt salts of substituted hydroxyformamidines of the type $R_1\cdot N\cdot CR\cdot NR'\cdot OH$, attention must be given to the following points: (1) the salts are normal and have the metal attached to oxygen (compare Abstr., 1905, i, 175); (2) they have the same colour in solution as in the solid state; (3) they retain the basic character of the parent hydroxyformamidine; (4) they have normal molecular weights in chloroform; (5) potassium hydroxide does not precipitate the metallic hydroxide; (6) azohydroxyamides, hydroxyamidoximes, and hydroxyguanidines, which form similar abnormally coloured salts, all contain the group $N:X\cdot N\cdot OH$.

The behaviour of these salts recalls that of internally complex metallic salts (compare Schiff, Abstr., 1898, i, 243; Bruni and Fornara, Abstr., 1904, i, 855). If the assumption is made that, in the salts of amino-acids, the metal, attached to oxygen, is also bound by residual affinity to the aminic nitrogen atom, a parallelism can be drawn between the abnormally coloured metallic salts of amino-acids and the metal-ammonia compounds. The salts of hydroxyformamidines would thus be formulated,  $R\cdot C\begin{smallmatrix} \nearrow NR— \\ \searrow NR'O \end{smallmatrix}\!\!>M$. (For change of colour in complex salt formation, compare Tschugaeff, Abstr., 1905, i, 865.) Abnormal light absorption seems to be connected with the presence of the metal in the group $\cdot NH\cdot OM$ containing a singly-linked nitrogen atom, for benzenylamidoxime, $OH\cdot N{:}CPh\cdot NH_2$, and benzenylpiperidyloxime, $C_5NH_{10}\cdot CPh{:}N\cdot OH$, do not yield abnormal copper salts.

3-*Hydroxy*-1-*phenyl*-3-*benzylformamidine*, $NPh{:}CH\cdot N(OH)\cdot CH_2Ph$, m. p. 165° (decomp.), is obtained from β-benzylhydroxylamine and ethyl*iso*formanilide in absolute alcohol. It forms large, colourless, rhombic plates and exhibits feeble acid properties; the stable *hydrochloride* has m. p. 185—187° (decomp.). The *copper* salt, $(C_{14}H_{13}ON_2)_2Cu$, precipitated from an alcoholic solution of the hydroxyamidine by copper acetate, separates from toluene in reddish-brown scales; hydrogen chloride precipitates from its chloroform solution the *hydrochloride*, $(C_{14}H_{13}ON_2)_2Cu,2HCl$, as a microcrystalline, yellow mass which turns brown in the air and is decomposed by water or dilute alcohol, regenerating the brown copper salt. The *nickel* salt, $(C_{14}H_{13}ON_2)_2Ni$, forms yellow leaflets, and the *cobalt* salt dark amethyst crystals. When warmed with acetic anhydride, the hydroxyamidine is transformed into the isomeric *s*-phenylbenzylcarbamide (compare Bamberger and Destraz, Abstr., 1902, i, 538). *Benzenylpiperidyloxime*, m. p. 136—137°, forms long, glistening needles. C. S.

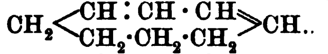
Abnormally Coloured Complex Metallic Salts of Acid Imides. HEINRICH LEY and F. WERNER (*Ber.*, 1907, 40, 705—707. Compare Abstr., 1906, i, 561; preceding abstract.).—In support of the theory that abnormal light absorption is exhibited by complex metallic salts in which the metal and nitrogen are united by residual affinities, the authors show that the copper salts of succinimide, camphorimide, phthalimide, and dibenzamide are blue, whilst under definite conditions complex salts of the type $[(RN)_2Cu(NR)_2]K_2$ (where $NR =$ acid imide) are obtained which exhibit abnormal colour.

Potassium copper camphorimide has been described (*loc. cit.*).

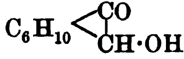
Potassium copper phthalimide, $(C_8H_4O_2N)_4CuK_2,4H_2O$, is obtained as a reddish-violet precipitate by adding aqueous copper acetate slowly to aqueous potassium phthalimide. Copper dimethylmaleimide forms sky-blue crystals, whilst the complex sodium copper compound is violet-red. C. S.

Tetramethylarsonium Iodide and its Pharmacological Action. EMIL BÜRGI (*Chem. Zentr.*, 1907, i, 152; from *Arch. exp. Path. Pharm.*, 56, 101—114).—Tetramethylarsonium iodide, $AsMe_4I$, prepared by heating arsenic with methyl iodide at 220° for twenty-four hours, is a white substance which slowly becomes reddish-brown when exposed to light and crystallises from methyl alcohol in tetrahedra; it gives coloured precipitates with many metallic salts.

The paralytic action of tetramethylarsonium iodide on the nervecentres resembles that of curare; it does not affect the heart of a frog or rabbit. Since in the case of a rabbit only a small portion is decomposed, the rest passing unchanged into the urine, the specific action of arsenic is not apparent. E. W. W.

The *cyclo*Octane Series. II. RICHARD WILLSTÄTTER and HANS VERAGUTH (*Ber.*, 1907, **40**, 957—970. Compare Abstr., 1905, i, 515).—The *cyclo*octadiene previously described readily yields a *dihydrobromide*, and the readiness with which the hydrocarbon polymerises is in harmony with the presence of conjugated double linkings,  $CH_2<\begin{matrix}CH:CH\cdot CH\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}>CH$. When the hydrobromide is heated with quinoline, or solid potassium hydroxide, it yields a much more stable unsaturated hydrocarbon, termed β-cyclo*octadiene*, which is readily reduced by Sabatier and Senderens's method (Abstr., 1901, i, 195, 459) to the saturated cyclic compound cyclo*octane*, C_8H_{16}. The presence of an eight-member ring in these compounds is confirmed by the fact that, when oxidised with nitric acid, the saturated hydrocarbon gives a good yield of suberic acid.

In the preparation of the dihydrobromide a certain amount of a *monohydrobromide*, $C_8H_{13}Br$, is formed; this can be separated by fractional distillation, and when heated with quinoline yields a dicyclo*octene*, C_8H_{12}. The position of the bridge in this compound has not been established. It is highly probable that a bridged compound is present in the original a-*cyclo*octadiene, as the proportions of mono- and dihydrobromide are always as 1 : 6. *dicyclo*Octene, when oxidised with permanganate, yields a crystalline *a-hydroxyketone*,



$$C_6H_{10}<\begin{matrix}CO\\ |\\ CH\cdot OH\end{matrix},$$

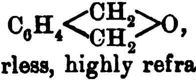
which, on further oxidation with chromic acid, yields an acid.

a-cyclo*Octadiene dihydrobromide*, $C_8H_{14}Br_2$, obtained by means of an acetic acid solution of hydrogen bromide, is a colourless, viscid oil with a sweet odour and b. p. 150—151°/12·5 mm. (corr.), D_4^0 1·662. On exposure to the air it turns to a pink colour, and finally to a dark steel-blue with a reddish-violet fluorescence.

A small amount of a *tetrabromo*cyclo*octane*, $C_8H_{12}Br_4$, has been prepared by the action of excess of bromine on the dihydrobromide in presence of iodine or iron. It crystallises in pointed prisms, m. p. 132·5°.

β-cyclo*Octadiene* is a colourless, mobile liquid, b. p. 143—144°, and D_4^0 0·887. It has an odour of tropilidine and gives an intense orange coloration with concentrated sulphuric acid.

Small amounts of naphthalene are formed when the dihydrobromide is heated with quinoline at a high temperature, and the same hydrocarbon is produced when *o*-xylylene bromide is heated at 260—270° with quinoline, whereas when *o*-xylylene bromide is heated with potassium hydroxide o-*xylylene oxide*,



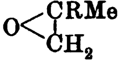
$$C_6H_4<\begin{matrix}CH_2\\ CH_2\end{matrix}>O,$$

is formed. This is a colourless, highly refractive oil, b. p. 192° (corr.), D_4^0 1·098, and has an odour of bitter almonds.

The *hydrobromide* of *dicyclo*octene, $C_8H_{13}Br$, is a clear, viscid liquid, b. p. 92·5—93°/15 mm., D^0_4 1·330, and has a sweet odour. It is stable towards permanganate, but in contact with the air yields black products. dicyclo*Octene*, C_8H_{12}, is a colourless, mobile liquid of high refractive power, b. p. 137·5—139° (corr.), D^0_4 0·9097, and has an odour of tropilidene.

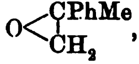
The *hydroxy-ketone*, $C_8H_{12}O_2$, crystallises in needles, m. p. 65—65·5°, and yields a *semicarbazone* which decomposes at 251°.

cyclo*Octane* is a colourless liquid with an odour resembling camphor, b. p. 146·3—148°, D^0_4 0·849, and D^{20}_4 0·833, and when cooled solidifies. A slightly impure fraction, b. p. 145·3—146·3°, D^0_4 0·850, D^{20}_4 0·835, was also obtained, but would not solidify. J. J. S.

Benzene Hydrocarbons containing a ψ-Allyl Side Chain; Methoethenylbenzene [β-Allylbenzene] and its Homologues. Study of some Molecular Migrations. Part I. Benzene Hydrocarbons containing a ψ-Allyl Side Chain. Max Tiffeneau (*Ann. Chim. Phys.*, 1907, [viii], 10, 145—198).—A detailed account of the preparation, properties, and derivatives of hydrocarbons of the type $R{\cdot}CMe{:}CH_2$, where R denotes the phenyl or *o*-, *m*-, or *p*-tolyl group. The hydrocarbons, prepared by dehydrating the corresponding dimethylcarbinol, $R{\cdot}CMe_2{\cdot}OH$, are reduced by the action of sodium and alcohol to the hydrocarbon $R{\cdot}CHMe_2$, or directly by hydrogen in the presence of nickel to form the completely saturated hydrocarbon; they are oxidised directly by oxygen to form trioxymethylene and the corresponding ketone, $R{\cdot}COMe$, which is also the chief product when permanganate is the oxidising agent employed; they react with chlorine or bromine to form the saturated derivatives, $R{\cdot}CMeX{\cdot}CH_2X$ (where X denotes Cl or Br), which, on treatment with alcoholic potash, yield the monohalogen derivatives, $R{\cdot}CMe{:}CHX$. These hydrocarbons furnish halohydrins of the type $R{\cdot}CMe(OH){\cdot}CH_2X$, either by direct union with hypochlorous, hypobromous, or hypoiodous acid, or more conveniently by the action of magnesium methyl bromide or iodide on the monohalogen derivative of acetone; the chloro- or iodo-hydrins condense with dimethyl- or diethyl-amine to form substituted carbinols of the type $R{\cdot}CMe(OH){\cdot}CH_2{\cdot}NAr_2$ (where Ar denotes Me or Et), which yield characteristic methiodides, benzoyl or cinnamyl derivatives; the iodohydrins react with potassium hydroxide to form the corresponding methylene oxide,  $O{<}\begin{matrix}CRMe\\ |\\ CH_2\end{matrix}$, and when treated with silver nitrate lose hydrogen iodide and undergo a molecular migration with the formation of a substituted acetone according to the equation: $R{\cdot}CMe(OH){\cdot}CH_2I \longrightarrow HI + R{\cdot}CH_2{\cdot}COMe$.

β-Allylbenzene.—The preparation, properties, and most of the derivatives of this hydrocarbon have already been described (Abstr., 1902, i, 433, 449; 1903, i, 81; 1904, i, 63; 1905, i, 523; 1906, i, 965); the following facts are new: β-allylbenzene, b. p. 161—162°, 60—61°/17 mm., or 68—69°/27 mm., D^0 0·9278 or D^{21} 0·9085, yields the dimeride, $C_{18}H_{20}$ (compare Grignard, Abstr., 1901, i, 681), m. p. 51—52°, b. p. 163—164°/14—15 mm. or 299—300°, when treated with sulphuric acid, or when a slight excess of methyl iodide is used in the preparation of the hydrocarbon in which case the polymeride, $C_{18}H_{20}$, b. p. 175°/16 mm., D^0 1·012, is also formed (compare Klages, Abstr., 1902, i, 666); the *dichloride*, $CPhMeCl\cdot CH_2Cl$, b. p. 115—125°/8 mm., yields *β-chloro-a-methylstyrene*, $CPhMe\colon CHCl$, b. p. 210—215° or 102—106°/14 mm.; the chlorohydrin, b. p. 124—125°/17 mm., D^0 1·168 yields with dimethylamine, phenylmethyldimethylaminomethylcarbinol (compare Fourneau, Abstr., 1904, i, 377), and with diethylamine, *phenylmethyldiethylaminomethylcarbinol*,

$$OH\cdot CPhMe\cdot CH_2\cdot NEt_2,$$

b. p. 244—247° or 138—140°/22 mm., the *cinnamyl* derivative has m. p. 190—192°. The *bromohydrin* $OH\cdot CPhMe\cdot CH_2Br$, b. p. 141°/19 mm., D^0 1·413; the iodohydrin, b. p. 144—145°/12 mm., D^0 1·541, yields the oxide,  $O\!<\!\begin{matrix}CPhMe\\ |\\ CH_2\end{matrix}$, which has D^{26} 1·024, n_D^{26} 1·5161.

o-*Methoethenyltoluene* [o-*β-allyltoluene*], $C_7H_7\cdot CMe\colon CH_2$. The starting point of this hydrocarbon is o-*tolyldimethylcarbinol*, m. p. 41°, b. p. 217—218° or 116°/22 mm., which is obtained by the action of magnesium *o*-tolyl bromide on acetone, or magnesium methyl iodide on methyl *o*-toluate. When distilled with oxalic acid, it yields o-*β-allyltoluene*, b. p. 168—169°, D^0 0·9076, which on oxidation with permanganate forms o-*tolyl methyl ketone*, b. p. 216°, and the iodohydrin yields o-*tolylacetone*, b. p. 227°, the *oxime*, m. p. 75°, and the semicarbazone, m. p. 181°.

m-*Methoethenyltoluene* [m-*β-allyltoluene*], $C_7H_7\cdot CMe\colon CH_2$, b. p. 183—185°, D^0 0·9115, yields *m*-tolyl methyl ketone on oxidation, b. p. 218—220°, D^{20} 0·989, (oxime, m. p. 94°), and *m*-cymene on reduction, b. p. 174—176°, D^{20} 0·862; the *iodohydrin* reacts with silver nitrate to form m-*tolylacetone*, $C_7H_7\cdot CH_2\cdot COMe$, b. p. 228—229°, D^0 1·019; the *semicarbazide* has m. p. 139°.

p-Methoethenyltoluene [*p*-*β*-allyltoluene], $C_7H_7\cdot CMe\colon CH_2$, is a colourless, mobile liquid with an odour of thyme, b. p. 184—185° (Errera, Abstr., 1891, 1021, gives 198—200°), D^0 0·9122; it yields *p*-cymene, b. p. 174—176, D^{15} 0·860 on reduction, and *p*-tolyl methyl ketone (oxime, m. p. 88°) on oxidation; the *dibromide* is liquid even at − 15°, and yields the *glycol*, $C_7H_7\cdot CMe(OH)\cdot CH_2\cdot OH$, m. p. 32°, when treated with barium carbonate. The *dimeride*, $C_{20}H_{24}$, has m. p. 40°; the *iodohydrin* reacts with yellow mercuric oxide to form p-*tolylacetone*, $C_7H_7\cdot CH_2\cdot COMe$, b. p. 232—233°, D^0 1·007 (the *oxime* has m. p. 90° and the semicarbazone, m. p. 158°), and with dimethylamine to form *p*-tolylmethyldimethylaminomethylcarbinol,

$$C_7H_7\cdot CMe(OH)\cdot CH_2\cdot NMe_2,$$

b. p. 253—255° or 135—136°/18 mm., D^0 0·982. M. A. W.

Reductions with Amorphous Phosphorus. II. THEODOR WEYL (*Ber.*, 1907, 40, 970—974. Compare this vol., i, 118).—When nitrobenzene is dropped into a boiling mixture of sodium hydroxide solution and red phosphorus, the only reduction product which can be isolated is aniline. The yield is not good, as a large amount of unaltered nitrobenzene is always found. The products formed when the mixture of nitrobenzene, sodium hydroxide solution, and red phosphorus is heated in a reflux apparatus at 140—170°, consist of aniline, azoxybenzene, and azobenzene, in certain experiments as much as 50% of the nitrobenzene being converted into azobenzene. Calcium hydroxide and ammonium hydroxide are not so efficient as sodium and potassium hydroxides, and the substitution of 95% alcohol for water retards the reduction.

When the reacting substances are heated in sealed tubes at 100—150° the amount of reduction is small, but at 170°, with soda lime and water, some 21% of aniline and 6% of azoxybenzene are formed.

It has been found that phosphine is evolved by the action of ammonium hydroxide solution on amorphous phosphorus. J. J. S.

Dichlorodiphenylsulphone. FRITZ ULLMANN and JOHANNES KORSELT (*Ber.*, 1907, **40**, 641—648).—Beckurt and Otto's 4:4′-dichlorodiphenylsulphone (Abstr., 1879, 243) is converted quantitatively into 4 : 4′-*dichloro*-3 : 3′-*dinitrodiphenylsulphone*, $(NO_2\cdot C_6H_3Cl)_2SO_2$, by a mixture of equal volumes of nitric acid (D 1·5) and sulphuric acid at 100°. It crystallises from glacial acetic acid in long, glistening needles, m. p. 202°. 4 : 4′-*Dichloro*-3 : 5 : 3′-*trinitrodiphenylsulphone*, $C_{12}H_5O_8N_3Cl_2S$, obtained when fuming sulphuric acid (40% SO_3) is used at 150° for a short time, forms almost colourless needles, m. p. 220°, whilst the 3 : 5 : 3 : 5′-*tetranitro*-derivative, $C_{12}H_4O_{10}N_4Cl_2S$, pale yellow needles, m. p. 290°, is the product obtained when the heating is continued for two hours at 150° and 60% SO_3 sulphuric acid is employed.

Alcoholic solutions of all these nitro-compounds, on being boiled with aniline, lose the two chlorine atoms and give dianilino-derivatives. 3 : 3′-*Dinitro*-4 : 4′-*dianilinodiphenylsulphone*, $C_{24}H_{18}O_6N_4S$, forms orange-red crystals from benzene, m. p. 260° ; the corresponding *trinitro*- and *tetranitro*-compounds are also orange-red, and have m. p. 210° and 250°.

3 : 3′-Dinitro-4 : 4′-dihydroxydiphenylsulphone and its methoxy- and ethoxy-derivatives are obtained by the interaction of alcoholic sodium hydroxide, methoxide, or ethoxide, and the dinitrodichlorosulphone (Annaheim, this Journ., 1874, 795). The 3 : 5 : 3′ : 5′-tetranitro-4 : 4′-dihydroxy-derivative is obtained in a similar manner (Annaheim, Abstr., 1879, 294).

3 : 3′-*Diamino*-4 : 4′-*dianilinodiphenylsulphone*, $C_{24}H_{22}O_2N_4S$, crystallising from alcohol in colourless plates, m. p. 186°, gives a phenazonium derivative with 2 mols. of phenanthraquinone in the presence of hydrogen chloride.

When dichlorodinitrodiphenylsulphone is heated with alcoholic ammonia for four hours at 150°, yellow octahedra of 3 : 3′-*dinitro*-4 : 4′-*diaminodiphenylsulphone*, $C_{12}H_{10}O_6N_4S$, m. p. 309°, are formed. The *tetra-amino*-derivative obtained on reduction forms colourless leaflets, m. p. 174°.

Annaheim's dinitrohydroxyanilinodiphenylsulphone (this Journ., 1874, 697) is shown to be an additive compound of the dinitrodihydroxydiphenylsulphone (1 mol.) with aniline (2 mols.). W. R.

Nature of the Carbon Double Linking II. Addition of Bromine. Hugo Bauer and H. Moser (*Ber.*, 1907, **40**, 918—924. Compare Abstr., 1905, i, 729; 1904, i, 841).—The interaction of ethenoid compounds and bromine in solution is of the second order (compare Herz and Mylius, this vol., i, 55; Plotnikoff, Abstr., 1906, ii, 12), but the constants obtained vary, especially the first values; this is perhaps explained by the formation of perbromides. The experiments were carried out in the dark in blackened vessels, and it was found that the solvent exercised an important influence in promoting the change. With stilbene in chloroform, $v = 200$ t 29°, the reaction was complete in seven days, whereas in carbon tetrachloride fifty-five days were required. If, however, a methyl group is introduced instead of hydrogen, the reaction velocity is greatly accelerated, *a*-methylstilbene in chloroform taking thirty minutes, and in carbon tetrachloride requiring two days ($v = 200$ t 29°) for complete interaction with bromine.

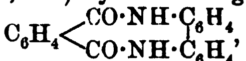
a-Phenylcinnamonitrile dibromide (m. p. 138°, V. Meyer and Frost, Abstr., 1889, 598, give 128°) dissociates slowly in carbon tetrachloride solution at 30° into nitrile and bromine; at 100° the velocity is much increased, so that the equilibrium established between bromine and nitrile was determined by using the dibromide to start with, and in the alternative the two interacting substances; the results obtained were the same by the two methods. In accordance with a reaction of the second order, dilution has a marked effect on the point of equilibrium; with $v = 200$ t 30°, 16·5% of dibromide is obtained; with $v = 400$ only 9%.

Light favours the production of dibromide, particularly red rays; only 4% of the bromine is taken up by *a*-phenyl-*o*-nitrocinnamonitrile in the dark, whilst in ordinary daylight 34% is absorbed.

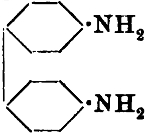
The reaction in the case of the stilbenes is practically complete; the introduction, however, of a nitrile group diminishes the reactivity of the ethenoid linking, as is also the case if a hydrogen atom in the phenyl nucleus is replaced by a nitro-group; K for *a*-phenylcinnamonitrile being 0·02112, $v = 200$, whereas for *a*-phenyl-*o*-nitrocinnamonitrile it is 0·01152. W. R.

Stereochemical Conceptions of Polycyclic Compounds. Felix Kaufler (*Annalen*, 1907, **351**, 151—160).—The usual formulæ for polycyclic compounds, either of the type of diphenyl or of that of conjugated ring systems, such as naphthalene, which represent the nuclei in one plane, may be displaced with advantage by stereochemical formulæ representing the manner in which the rings of the nuclei are inclined towards one another.

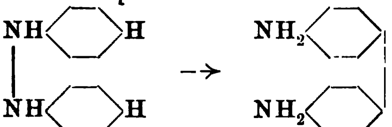
Materials on which may be based a stereochemical formula for diphenyl consist of the benzidine derivatives having the two amino-groups united by one or two carbon atoms, as in carbonylbenzidine (Michler and Zimmermann, Abstr., 1882, 182) or oxalylbenzidine (Strakosch, this Journ., 1872, **25**, 503). In consequence, however, of the difficulty of determining the molecular weights of such substances, the bimolecular formulæ could not be looked on previously as excluded. A determination of the molecular weight of Kolber's phthalylbenzidine (Abstr., 1904, i, 778) by the boiling point method now shows it to have the formula



$C_6H_4<\begin{matrix}CO\cdot NH\cdot C_6H_4\\ CO\cdot NH\cdot C_6H_4\end{matrix}$, and it appears probable that all such substances have unimolecular formulæ. The two amino-groups of benzidine must be much closer together than is represented by the usual formula $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, their relative positions being represented better by the stereochemical formula

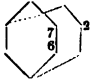


. This space formula explains the difficulty of diazotising the second amino-group and the slowness with which the second diazo-group couples as cases of steric hindrance. It also simplifies the conception of the "benzidine change" of hydrazobenzenes,



, or similarly of the conversion of tetraphenylhydrazine into *s*-diphenylbenzidine (Wielandt and Gambarjan, Abstr., 1906, i, 453).

It is found that 2 : 7-diaminonaphthalene forms only monosubstitution products when boiled with chlorotrinitrobenzene or chlorodinitrobenzene and potassium acetate in alcoholic solution. 7-*Trinitroanilino-2-naphthylamine*, $C_{16}H_{11}O_6N_5$, crystallises in yellow needles, m. p. 212°. 7-*Dinitroanilino-2-naphthylamine*, $C_{16}H_{12}O_4N_4$, crystallises in small, dark yellow needles, m. p. 227°. This is explained by mutual steric interference of the groups in positions 2 : 7, and is expressed in the spacial formula



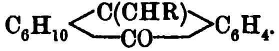
; this formula explains also the difference in the stability of naphthalene-2 : 6- and naphthalene-2 : 7-disulphonic acids.

Similar differences are observed between 2 : 6- and 2 : 7-disubstituted anthraquinones. Whilst sodium anthraquinone-2 : 6-disulphonate is converted into 2 : 6-diaminoanthraquinone by ammonia at 190°, sodium anthraquinone-2 : 7-disulphonate yields only 2-*aminoanthraquinone*-7-*sulphonic acid*, $C_{14}H_9O_5NS,H_2O$, which forms light yellow crystals; the *barium* salt, $(C_{14}H_8O_5NS)_2Ba,2H_2O$, crystallises in dark red leaflets; *sodium* 2-*acetylaminoanthraquinone*-7-*sulphonate*,

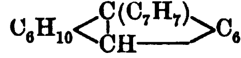
$$C_{16}H_{10}O_6NSNa,2\tfrac{1}{2}H_2O,$$

crystallises in orange-red leaflets. G. Y.

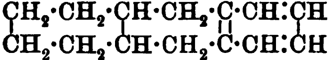
Constitution of Octahydroanthracene. Marcel Godchot (*Bull. Soc. Chim.*, 1907, [iv], 1, 121—129. Compare Abstr., 1904, i, 987; 1905, i, 201; 1906, i, 76, 494).—On oxidation with potassium permanganate in presence of water or acetone, octahydroanthracene yields phthalic acid. The hexahydroanthrone produced by oxidising the octahydride with chromic acid readily condenses in the presence of alkalis with aromatic aldehydes, forming compounds of the type



$$C_6H_{10}{<}\begin{matrix}C(CHR)\\CO\end{matrix}{>}C_6H_4.$$

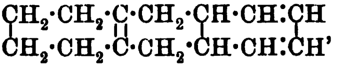
Benzylidenehexahydroanthrone, m. p. about 137—138°, forms faintly yellow, prismatic needles, and with bromine in presence of carbon disulphide furnishes a *dibromide*, m. p. 160° (decomp.), which crystallises in small, colourless prisms. On reduction with sodium and alcohol, benzylidenehexahydroanthrone furnishes 9-*benzyloctahydroanthranol*, m. p. 169°, which crystallises in large, colourless needles, and on distillation, even under reduced pressure, furnishes 9-*benzylhexahydroanthracene*,  $C_6H_{10}{<}\begin{matrix}C(C_7H_7)\\|\\CH\end{matrix}{>}C_6H_4$, b. p. 255—258°/20 mm., D^0 1·253, which does not crystallise at −20°, and unlike the foregoing substances yields solutions exhibiting a fine blue fluorescence. The *picrate*, m. p. 120°, forms yellow needles and is resolved into its generators by water. Benzylhexahydroanthracene is also formed when hexahydroanthrone is treated with magnesium benzyl chloride in presence of ether. *Anisylidenehexahydroanthrone*, m. p. about 152°, forms small, yellow tablets, and like its benzylidene analogue does not react with hydroxylamine or semicarbazide. *Cumylidenehexahydroanthrone*, m. p. 148°, forms small, yellow leaflets.

From these results the author concludes that this octahydroanthracene may be represented by the formula:



$$\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_2\cdot C\cdot CH{:}CH\\ CH_2\cdot CH_2\cdot CH\cdot CH_2\cdot C\cdot CH{:}CH\end{matrix}$$

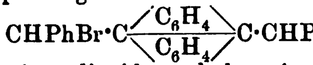
or



$$\begin{matrix}CH_2\cdot CH_2\cdot C\cdot CH_2\cdot CH\cdot CH{:}CH\\ CH_2\cdot CH_2\cdot C\cdot CH_2\cdot CH\cdot CH{:}CH\end{matrix},$$

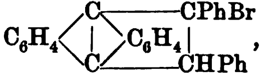
and of these the first is preferred, since it explains more easily the production of phthalic acid when the hydrocarbon is oxidised with potassium permanganate, and establishes an analogy between the formation of octahydroanthracene from anthracene and that of tetrahydronaphthalene from naphthalene (Leroux, Abstr., 1904, i, 986), both these reactions being brought about by Sabatier and Senderens's method of hydrogenation (Abstr., 1901, i, 459).

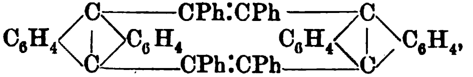
T. A. H.

Anthracene Series. EDUARD LIPPMANN and RODOLFO FRITSCH (*Annalen*, 1907, **351**, 52—64. Compare Abstr., 1904, i, 865).—II. *Dibromodibenzylanthracene and its Derivatives.*—Dibromodibenzylanthracene and a number of its derivatives have been prepared and compared with the corresponding monosubstituted dibenzylanthracenes. The *dibromo*-compound,  $CHPhBr\cdot C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}C\cdot CHPhBr$, prepared by passing a current of carbon dioxide and bromine vapour through dibenzylanthracene in carbon disulphide solution, forms yellow crystals, m. p. 212°, is only partially hydrolysed by boiling potassium hydroxide or carbonate, and does not react with moist silver oxide. The *diacetate*, $C_{32}H_{26}O_4$, m. p. 252°, prepared by the action of the dibromide on silver acetate in benzene, or on an alkali acetate in glacial acetic acid, solution, forms solutions with blue fluorescence, and when boiled with alcoholic potassium hydroxide yields the *monoacetate*, $OH\cdot C_{28}H_{20}\cdot OAc$, which crystallises in red needles, m. p. 216°, and forms solutions with bluish-red fluorescence. The *dibenzoate*, $C_{28}H_{20}(OBz)_2$, forms white crystals, m. p. 285°, and is only partially hydrolysed by boiling potassium hydroxide. The *dinitrate* forms light yellow crystals, m. p. 177° (decomp.), and when heated at 140—180° yields nitrogen dioxide, benzaldehyde, and anthraquinone. When boiled with alcohol in benzene solution, the dibromo-compound yields *diethoxydibenzylanthracene*, $C_{28}H_{20}(OEt)_2$, which forms white crystals, m. p. 220°, dissolves in benzene or chloroform with blue fluorescence and is not hydrolysed by sulphuric acid. The *dianilino*-derivative,

$$C_{14}H_8(CHPh\cdot NHPh)_2,$$

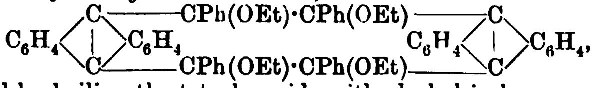
forms yellow crystals, m. p. 263° (decomp.).

III. *Degradation of Dibromodibenzylanthracene.*—The dibromo-differs from the monobromo-compound in that it does not yield hydrogen bromide when heated with quinoline in benzene solution, but resinifies at higher temperatures. An oxygen-free product could not be obtained by the decomposition of the *carbonate* formed by the action of the dibromo-compound on silver carbonate. On prolonged heating at 212°, the dibromo-compound yields hydrogen bromide and *bromodibenzylideneanthracene*,  , m. p. 99°, which is reduced to dibenzylanthracene by zinc dust and glacial acetic acid. The dibromo-compound is oxidised by phenylhydrazine in boiling benzene solution with formation of *bisdibenzoanthracene*,



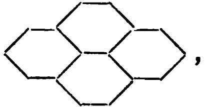
which separates from acetone in yellow crystals, m. p. 197°, decolorises potassium permanganate solution, and yields a *tetrabromide*, $C_{56}H_{36}Br_4$, forming yellow crystals, m. p. 215°, and reduced to bisdibenzylideneanthracene by means of zinc dust and acetic acid.

Bisdiethoxydibenzylideneanthracene,

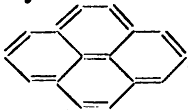


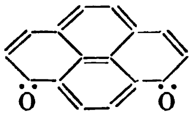
prepared by boiling the tetrabromide with alcohol in benzene solution, forms a white, crystalline mass, m. p. 218°. G. Y.

Structure of Pyrene. Guido Goldschmiedt (*Annalen*, 1907, 351, 218—232).—Although the investigation of the constitution of pyrene by Bamberger and Philip (Abstr., 1887, 271) established that the nucleus of this hydrocarbon has the structure,

 ,

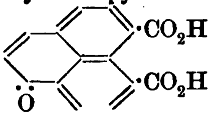
no satisfactory conclusion has been reached as to the distribution of the double linkings.

The author now shows by a series of experiments that the yellow colour of pyrene is that of the substance itself and not of some impurity, the colour disappearing only on change of the pyrene as in its reduction with sodium and amyl alcohol. Contrary to Graebe's statement (this Journ., 1871, 117, 690) pyrene does not become colourless when exposed to sunlight in benzene solution; the apparently colourless leaflets obtained on sublimation of pyrene (Hintz, *Inaug. Diss.*) are yellow when heaped together. The author quotes also the properties of a number of derivatives of pyrene in support of his view that the hydrocarbon is yellow. It follows that pyrene is represented best by the formula , in which only one of the four rings is a benzene nucleus, the others having quinonoid structures. To the deep-red pyrenequinone is ascribed the structure



,

which on oxidation yields yellow pyrenic acid,



,

and on further oxidation is converted into colourless naphthalenetetracarboxylic acid.

The conversion of pyrene into pyrenequinone is explained also with the aid of Thiele's partial valencies. G. Y.

A New Exception to Carnelley and Thomson's Rule. Solution Equilibrium between Aniline and *o*-Chloronitrobenzene. Robert Kremann (*Monatsh.*, 1907, **28**, 7—11).—Kremann and Rodinis (Abstr., 1906, ii, 268) found that aniline does not form additive compounds with *m*- or *p*-chloronitrobenzene. It is shown now that this is the case also with aniline and *o*-chloronitrobenzene, the melting point curve for mixtures of these two substances having one eutectic point at −18°, representing a mixture containing about 23% of *o*-chloronitrobenzene.

A comparison of the solubilities of the three chloronitrobenzenes discovers an exception to Carnelley and Thomson's rule (Trans., 1888, 53, 782) that in a group of isomeric organic substances the order of fusibility is the same as that of solubility, the most easily fusible substance being also the most soluble. The solubility curves of *o*- and *m*-chloronitrobenzenes follow this rule to the eutectic points, but that of the *p*-compound only to −2·5°, at which temperature it cuts the curve for the *m*-isomeride; at temperatures below −2·5°, the solubility of *p*-chloronitrobenzene is greater than that of the *m*-chloronitro-compound, although the latter melts at the lower temperature.

An analogous case is found in the solubilities of *p*- and *o*-dinitrobenzenes in aniline (Kremann and Rodinis, *loc. cit.*) which are identical at 10°; above this temperature, Carnelley and Thomson's rule holds good, but below 10° the ortho-isomeride, which has the lower melting point, is the less soluble. As *m*-dinitrobenzene forms with aniline a 1 : 1-molecular additive compound, it does not belong to the class of indifferent substances to which alone Carnelley and Thomson's rule is applicable. G. Y.

Preparation of ω-Chloroacetanilide and its Homologues. Alfred von Janson (D.R.-P. 175586).—α-Chloroacetanilide may be readily obtained by adding phosphorus trichloride or thionyl chloride to a warm mixture of aniline hydrochloride and chloroacetic acid; the product is poured into water and the substance crystallised from alcohol. Other salts of aniline and its homologues may be substituted for the foregoing hydrochloride and the condensation may also be effected with phosphorus pentachloride or oxychloride. G. T. M.

Preparation of Phenylglycine and its Homologues. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 175797).—Phenylglycine has now been prepared from chloroacetic acid and nitrobenzene in the following manner. Nitrobenzene containing about 10% of aniline is warmed at 70° with iron filings, and dilute chloroacetic acid is slowly introduced. The temperature of this acid should be gradually increased from 50° to 90°. The addition of the acid should suffice to keep the mixture boiling vigorously, and after two hours' heating at 98—100° the solution is neutralised with sodium carbonate. The aniline is distilled off and the phenylglycine isolated in the usual way. G. T. M.

Preparation of Phenylglycine and its Homologues. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 177491).—The ordinary processes for obtaining phenylglycine by condensing chloroacetic acid with aniline either in excess or with reagents for fixing hydrogen chloride are unsatisfactory, owing to the formation of by-products. This difficulty has now been overcome by operating in the presence of an oxide or a carbonate of a heavy metal by means of which the phenylglycine forms an insoluble salt and is thus removed from the sphere of action. Ferrous chloride is dissolved in water, decomposed with the requisite amount of an alkali, and the mixture heated to 90—100°; chloroacetic acid and aniline are quickly added successively and the heating continued for one and a half hours; after cooling, the precipitated iron salt of phenylglycine is collected and converted into phenylglycine in the usual way. Tolylglycine may be obtained similarly. G. T. M.

Action of Alkali Alkyloxides on Unsaturated Imides. II. Arnaldo Piutti (*Gazzetta*, 1906, **36**, ii, 723—734. Compare Abstr., 1906, i, 657).—The hydroxides of the alkali and alkaline-earth metals, with the exception of calcium, as well as all their derivatives with alcohol or acetone react with substituted imides of maleic, citraconic, and itaconic acids, giving intensely violet compounds which are insoluble in ether and are decolorised even in solution by the addition of water. In the present paper, the author describes the method used for obtaining certain of these compounds yielded by *p*-ethoxyphenylcitraconimide, the chief difficulty in their preparation being that of rendering and maintaining the reagents and solvents employed absolutely anhydrous.

With sodium ethoxide in alcoholic solution, *p*-ethoxyphenylcitraconimide gives the *compound* $C_{13}H_{13}O_3N,EtONa$, which is obtained as a reddish-violet powder, becoming soft at about 200° and remaining so up to 300°; water dissolves it, giving a reddish-violet solution which gradually becomes colourless; it is soluble also in alcohol with formation of an intense violet coloration which is weakened by addition of water; it is also soluble in amyl alcohol, ethyl acetate, and acetone.

The *compound* $C_{13}H_{13}O_3N,C_5H_{11}\cdot ONa$, formed with sodium amyloxide, is a reddish-violet powder, which softens at 95° and decomposes at 140—150°; its behaviour towards solvents resembles that of the preceding compound, and it is also soluble in toluene or benzene and sparingly so in xylene or carbon disulphide.

The *compound* $C_{23}H_{30}O_4NNa$, formed with sodium bornyloxide, is a reddish-violet powder, which softens at 180°, melts at 195—210°, and behaves towards solvents like the preceding compound.

With the sodium derivative of dimethylacetone, *p*-ethoxyphenylcitraconimide gives a *compound* $C_{16}H_{18}O_4NNa$, which forms a dark reddish-violet powder softening at 135° and melting at 170—160° (?); it is insoluble in benzene, toluene, or carbon disulphide, but towards other solvents it behaves like the borneol derivative. T. H. P.

Preparation of β-Naphthylamine-3:6:8-trisulphonic Acid.

KALLE & Co. (D.R.-P. 176621).—1-Nitronaphthalene-3 : 6 : 8-trisulphonic acid when heated at 150—170° for eight hours with concentrated ammonia yields β-naphthylamine-3 : 6 : 8-trisulphonic acid.

G. T. M.

Miscibility of Solutions of Phenols in Aqueous Alkalis with Organic Substances Insoluble in Water.

RUDOLF SCHEUBLE (*Annalen*, 1907, 351, 473—480).—In the course of an investigation of the behaviour of salicylic esters towards potassium hydroxide, the author observed that on boiling thymyl salicylate with the aqueous alkali an increase in the volume of the upper or ester layer took place at the expense of the aqueous solution until after a few minutes a point was reached when the two previously non-miscible layers became completely miscible. This phenomenon is explained by the further observations that a solution of much thymol in concentrated aqueous potassium hydroxide is a solvent for various organic substances otherwise insoluble in water, and that on addition of a certain amount of aqueous potassium hydroxide to the ternary mixture of potassium thymoxide, potassium hydroxide, and the potassium derivative of thymol salicylate, which is formed in the first case, two non-miscible layers are formed. The moment of mixing of the two layers on boiling is not that when the ester has been completely hydrolysed, but when its volume has been diminished in a certain proportion.

This property of thymol is common to all phenols and is known technically in the extraction of phenols from tar distillates, and in the preparation of disinfectants by solution of phenols in alkaline phenol or soap solutions. Contrary to the generally accepted view all phenols can be extracted from their alkaline solutions with more or less ease by ether.

Quantitative experiments show that the amount of phenol, *m*-cresol, *m*-4-xylenol, or carvacrol which must be added to a given amount of aqueous potassium hydroxide and octyl alcohol, toluene, or heptane to produce a clear solution increases for these three substances in the order named, and that the addition of water to 21·2% potassium hydroxide solution is at first without effect, but after a certain dilution is reached necessitates a rapid increase in the amount of phenol added.

On adding phenol to aqueous potassium hydroxide and octyl alcohol, the liquid becomes apparently homogeneous before the layers are miscible; this occurs in consequence of the two layers having the same refractive index. As this is strictly so only for light rays of a certain wave-length, the liquid exhibits a marked opalesence. G. Y.

Hydrolysis of Sodium Phenoxide. ALEXANDER NAUMANN, WILHELM MÜLLER, and EDUARD LANTELME (*J. pr. Chem.*, 1907, [ii], **75**, 65—87).—The method employed has been described (Abstr., 1906, ii, 732, 851). Similar results are obtained either by distilling 500 c.c. of the aqueous sodium phenoxide solution and collecting the distillate in 100 c.c. fractions or by distilling one litre of the solution and collecting the distillate in 25 c.c. fractions; from this the conclusion is drawn that the error due to the hydrolysis of further quantities of sodium phenoxide as phenol distils over, and the accumulation of an excess of sodium hydroxide in the distilled solution, is smaller than the experimental error.

To indicate the degree of hydrolysis of sodium phenoxide, the following numbers may be quoted. Aqueous solutions of concentration 1·0, 0·2, 0·1, 0·05, 0·01, and 0·002 mol. per litre are hydrolysed to the extent of approximately 4·4, 8·7, 11·6, 16·0, 29·7, and 56·4% respectively. The presence of a small excess of sodium hydroxide prevents to a great degree the hydrolysis of sodium phenoxide, especially in concentrated solutions. W. H. G.

Optical Resolution by Means of Dextrose. MARIO BETTI (*Gazzetta*, 1906, **36**, ii, 666—669. Compare Abstr., 1906, i, 950).—Racemic α-aminobenzyl-β-naphthol can be resolved into its optical isomerides by means of dextrose, which forms, with the *d*- and *l*-compounds, derivatives exhibiting different solubilities in alcohol.

The *dextrose* derivative of d-*α-aminobenzyl-β-naphthol*,

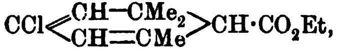
$$C_6H_{12}O_5{:}N{\cdot}CHPh{\cdot}C_{10}H_6{\cdot}OH,$$

which is the less readily soluble in alcohol, crystallises from this solvent in tufts of white, silky needles, m. p. 192° (decomp.). The l-*α-aminobenzyl-β-naphthol dextrose* compound crystallises from alcohol in minute, shining needles, m. p. 163—165° (decomp.). These dextrose derivatives may be converted into the corresponding α-aminobenzyl-β-naphthols (*loc. cit.*) by hydrolysis with hydrochloric acid. T. H. P.

Preparation of Aromatic Alcohols by the Electrolytic Reduction of Aromatic Acids. CARL METTLER (D.R.-P. 177490. Compare Abstr., 1906, i, 497).—The aromatic acids may be readily reduced to the corresponding alcohols when they are electrolysed in an alcoholic sulphuric acid solution with cathodes having a high supertension. Benzoic acid (200 parts) dissolved in 700 parts of alcohol and 300 parts of concentrated sulphuric acid was electrolysed at 20—30° with a current having a density of 6—12 amperes per 100 square centimetres of cathode surface. The electrodes were of lead, and the anode compartment contained dilute sulphuric acid. During the operation, a further amount (200 parts) of benzoic acid was added and a quantitative yield of benzyl alcohol was obtained. When reduced in a similar manner, *m*- and *p*-hydroxybenzoic acids furnished the corresponding hydroxybenzyl alcohols; 3 : 5-dichlorosalicylic acid gave rise to 3 : 5-dichlorosaligenin, and anthranilic and *m*-nitrobenzoic acids yielded respectively *o*-aminobenzyl alcohol and *m*-aminobenzyl alcohol. G. T. M.

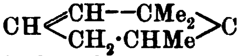
Oxidation of Cholesterol. Oxycholesterol; Chollanic Acid. ISAAC LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1907, 50, 436—439. Compare Darmstädter and Lifschütz, Abstr., 1898, i, 470).—The oxidation of cholesterol by dilute permanganate in concentrated acetic acid occurs in three stages. The products of the first two stages are yellow, amorphous, neutral resins; they have no definite melting points and dissolve readily in all solvents with the exception of water. The first product dissolves in a mixture of acetic and sulphuric acids, yielding a red to reddish-violet coloured solution with a characteristic absorption spectrum. The second product, *oxycholesterol*, yields under similar conditions a green solution. The final product, *chollanic acid*, $C_{26}H_{40}O_4$, is a dibasic acid, obtained as a colourless, curdy precipitate on the addition of a large excess of mineral acid to solutions of its salts. Although insoluble in water, it readily forms an emulsion with acid-free water and then cannot be filtered. The *calcium* salt, $C_{26}H_{38}O_4Ca$, has been prepared. All three oxidation products occur in wool fat. J. J. S.

Preparation of Δ⁴-*cyclo*Geranic Acid (1 : 3 : 3-Trimethyl*cyclo*-Δ⁴-hexene-2-carboxylic Acid). GEORG MERLING (D.R.-P. 175587).—*Ethyl chlorodehydro*-$\Delta^{2:4}$-cyclo*geranate*,



$$\mathrm{CCl}{<}\substack{\mathrm{CH{-}CMe_2}\\ \mathrm{CH{=}CMe}}{>}\mathrm{CH\cdot CO_2Et},$$

is prepared by treating ethyl *iso*phoronecarboxylate with phosphorus pentachloride and distilling the oily product under diminished pressure, when the ester is obtained as a colourless, inodorous oil, b. p. 108°/6 mm. It reduces ammoniacal silver nitrate, and on treatment with alcoholic potash yields chlorodehydro-$\Delta^{2:4}$-*cyclo*geranic acid, which separates from benzene or ethyl acetate in lustrous, colourless prisms.



Δ^4-cyclo*Geranic acid*, $CH{<}\begin{matrix}CH{-}{-}CMe_2\\CH_2{\cdot}CHMe\end{matrix}{>}CH{\cdot}CO_2H$, results from the reduction of chlorodehydro-$\Delta^{2\,4}$-*cyclo*geranic acid with sodium and ethyl alcohol; it is readily soluble in the ordinary organic solvents, and separates from ethyl acetate or light petroleum in well-defined lustrous prisms, m. p. 102—102·5°, b. p. 123·5°/6 mm.

Ethyl Δ^4-*cyclo*geranate is obtained either by ethylating potassium Δ^4-*cyclo*geranate or by reducing ethyl chlorodehydro-$\Delta^{2:4}$-cyclogeranate, b. p. 94°/6 mm. Δ^4-cyclo*Gerananilide*, $C_9H_{15}CO{\cdot}NHPh$, forms colourless needles, m. p. 157—158°. G. T. M.

Behaviour of Aromatic Esters towards Phosphorus Pentabromide and Pentachloride. WILHELM AUTENRIETH and PAUL MÜHLINGHAUS (*Ber.*, 1907, **40**, 744—751. Compare Abstr., 1895, i, 511; this vol., i, 31).—The methods of the earlier research have been extended to a number of aromatic and fatty aromatic esters which have been allowed to react directly with the phosphorus haloids at ordinary pressures without the medium of a solvent, moisture being carefully excluded. In most of the cases investigated the esters were easily chlorinated or brominated in the phenyl or naphthalene nucleus, more so in fact than the corresponding phenyl alkyl ethers.

Phenyl acetate and phosphorus pentabromide form a *monobromophenyl acetate*, a colourless liquid, b. p. 235—240° or 129—130°/15 mm., which, when hydrolysed, yields *p*-bromophenol. Small quantities of tri-*p*-bromophenyl phosphate are also obtained.

Phenyl benzoate (1 mol.) and phosphorus pentabromide (2 mols.) yield *dibromophenyl benzoate*, crystallising in long needles, m. p. 96—98°, which, on hydrolysis, forms 2 : 4-dibromophenol.

a-Naphthyl benzoate, glistening plates, m. p. 56°, prepared by shaking *a*-naphthol dissolved in sodium hydroxide with benzoyl chloride, only reacts with phosphorus pentachloride when heated for some hours in an oil-bath at 130—160°. The product, *monochloro-a-naphthyl benzoate*, forms glistening needles, m. p. 100—101°, and on hydrolysis gives a compound, m. p. 118°, crystallising from hot water in long, glistening needles, and probably identical with 4-chloro-1-naphthol (Reverdin and Kaufmann, Abstr., 1896, i, 175). With phosphorus pentabromide, *a*-naphthyl benzoate reacts more readily, and on warming a molecular mixture of the two, 4-*bromo*-1-*naphthyl benzoate*, plates, m. p. 105—106°, is obtained, since on hydrolysis it yields 4-bromo-1-naphthol (Reverdin and Kaufmann, *loc. cit.*). It forms an ethyl ether, crystallising in needles, m. p. 48°, identical with that obtained from the action of phosphorus pentabromide on *a*-naphthyl ethyl ether (this vol., i, 31).

β-Naphthyl benzoate and phosphorus pentachloride interact when heated at 130° to form the 1-chloro-2-naphthyl benzoate already obtained by Autenrieth.

β-Naphthyl benzoate and phosphorus pentabromide interact very readily and with considerable violence to form 1-bromo-2-naphthyl benzoate, which on hydrolysis forms a product crystallising in needles, m. p. 74°, whereas Armstrong (*Ber.*, 1882, 206) gives 84° for 1-bromo-2-naphthol.

Methyl benzoate and phosphorus pentachloride react first at

160—180° on distillation of the reaction mixture; 11 grams of benzoyl chloride were obtained from 20 grams of ester. E. F. A.

Formation of Chains from Aromatic Amino-Acids. Hans Meyer (*Annalen*, 1907, **351**, 267—282).—*o*-Aminobenzoylanthranilic acid (Anschütz, Schmidt, and Greiffenberg, Abstr., 1903, i, 57) being now readily obtainable (Mohr and Köhler, Abstr., 1906, i, 359; Meyer, *ibid.*, i, 432), the author has investigated its use in the formation of chains. The method of synthesis adopted is the formation of the nitrobenzoyl derivative of the amino-acid by the action of *o*-nitrobenzoyl chloride on the alkali, usually the lithium, salt of the amino-acid, and reduction of the resulting nitrobenzoyl compound with titanium trichloride (Knecht and Hibbert, Abstr., 1903, ii, 509). The solubility of the acid and basic salts of the amino-acids synthesised in this manner decreases with increasing molecular weight; *m*- and *p*-nitrobenzoylanthranilic acids are less soluble than the *o*-compounds.

o-Nitrobenzoylanthranilic acid, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, forms a colourless, crystalline mass, m. p. 239°, becoming yellow on exposure to air. *Methyl* o-*aminobenzoylanthranilate*,

$$NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Me,$$

crystallises in colourless needles, m. p. 118—119°. *o-Nitrobenzoylanthranilylanthranilic acid*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H,$$

forms almost colourless crystals, m. p. 224°, evolving gas. *Dianthranilylanthranilic acid*,

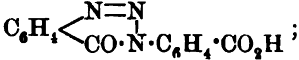
$$NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H,$$

forms slightly yellow needles, m. p. 228°, evolving gas. *o-Nitrobenzoyldianthranilylanthranilic acid*, $NO_2\cdot C_6H_4\cdot[CO\cdot NH\cdot C_6H_4]_3\cdot CO_2H$, is obtained as a white, microcrystalline powder, decomposing at 170—200°. *Trianthranilylanthranilic acid*,

$$NH_2\cdot C_6H_4\cdot CO\cdot[NH\cdot C_6H_4\cdot CO]_2\cdot NH\cdot C_6H_4\cdot CO_2H,$$

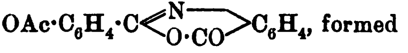
forms a dirty-white, gelatinous mass, which decomposes when heated.

When treated with sodium nitrite in acid solution, anthranilylanthranilic acid gives an intense yellow coloration; this is probably due to the *nitroso*-derivative, $NH_2\cdot C_6H_4\cdot CO\cdot N(NO)\cdot C_6H_4\cdot CO_2H$, which loses water, forming the colourless 3-*o-carboxyphenylphenotriazone*,



$$C_6H_4{<}\begin{array}{l}N{=}N\\ \quad\ |\\ CO\cdot N\cdot C_6H_4\cdot CO_2H\end{array};$$

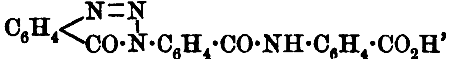
this separates from methyl alcohol in stout crystals, m. p. 192° (decomp.), explodes when heated, and if boiled with dilute hydrochloric or sulphuric acid, evolves nitrogen and forms o-*hydroxybenzoylanthranilic acid*, $OH\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, which crystallises in colourless needles, m. p. 212° (compare Mehner, Abstr., 1901, i, 470). The *acetoxyanhydride*,



$OAc\cdot C_6H_4\cdot C{<}\begin{array}{c}N\text{———}\\ O\cdot CO\end{array}{>}C_6H_4$, formed by boiling the hydroxy-acid with acetic anhydride and a small amount of sulphuric acid (compare Angeli and Angelico, Abstr., 1901, i, 45), crystallises in long needles, m. p. 154°. The phenotriazone is reduced by titanium chloride in alcoholic hydrochloric acid solution, forming benzoylanthranilic acid.

In concentrated hydrochloric acid solution, the phenotriazone must have the structure $NCl:N\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, in which state it couples with phenols, forming for instance with β-naphthol a scarlet dye; this is remarkable as hydroxyazo-dyes have been prepared exclusively in alkaline or neutral solution.

3-o-*Carboxyphenyl*-o-*carbamylphenylphenotriazone*,



$$C_6H_4<\begin{matrix}N{=}N\\ CO\cdot N\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H\end{matrix}$$

formed from dianthranilylanthranilic acid, separates from methyl alcohol in colourless crystals, m. p. 201° (decomp.), and yields a *dye* on prolonged boiling with β-naphthol and dilute hydrochloric acid.

G. Y.

Copper Salts of α-Aminophenylacetic Acid. George L. Stadnikoff (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 943—949. Compare Tiemann and Friedländer, Abstr., 1880, 473; 1882, 56).—For the purpose of characterising the amino-acids, the author has commenced a study of the copper salts of these acids.

The method given by Tiemann (*loc. cit.*) for preparing copper salts of α-aminophenylacetic acid yields compounds containing amounts of copper varying with the proportions of ammonia, copper sulphate, and amino-acid employed. The author dissolved a weighed quantity of α-aminophenylacetic acid in excess of ammonia solution and added to the liquid the corresponding amount of standard copper sulphate solution, the excess of ammonia being afterwards removed in a vacuum at 50—60°. In this way the following three compounds were obtained.

The *normal* salt, $(NH_2\cdot CHPh\cdot CO_2)_2Cu,H_2O$, separates in small, pale-blue crystals insoluble in water, but soluble in ammonia solution.

The *basic* salt, $NH_2\cdot CHPh\cdot CO_2\cdot Cu\cdot OH,H_2O$, forms small, sky-blue crystals, is insoluble in water, but readily soluble in ammonia solution, and deposits cupric oxide when suspended in water and boiled.

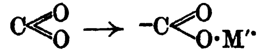
The *complex* salt, $(Cu:N\cdot CHPh\cdot CO_2)_2Cu,CuSO_4,3H_2O$, is deposited as a pale-blue powder, dissolves in dilute hydrochloric acid or excess of ammonia solution, and is decomposed by boiling water with formation of cupric oxide.

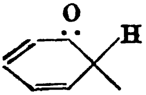
T. H. P.

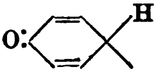
Isomeric Cinnamic Acids. Emil Erlenmeyer, jun., C. Barkow, and O. Herz (*Ber.*, 1907, **40**, 653—663. Compare Erlenmeyer, jun., and Barkow, Abstr., 1906, i, 429).—The authors have endeavoured to ascertain what part the brucine plays during the union of the base with *allo*cinnamic acid. This acid does not form a stable brucine salt from which the *allo*cinnamic acid can be regenerated; Liebermann's *iso*cinnamic acid and Erlenmeyer, jun's., *iso*cinnamic acid are those obtained (Abstr., 1905, i, 646, 892). Although these two acids melt at the same temperature, 59°, and have the same crystalline form, they are not enantiomorphously related. The hypothesis that *allo*cinnamic acid is a racemic mixture of these two acids has been abandoned, as, under the conditions employed, isodynamic change is likely to occur.

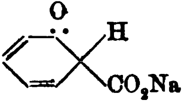
The brucine salt, m. p. 151°, is the normal salt, and crystallises in the tetragonal system $[a:c=1:1\cdot 7627]$. This salt undergoes isomeric change when recrystallised from absolute alcohol, the crystals obtained from the syrup have m. p. 70—75°, and yield Erlenmeyer's, sen's., *iso*cinnamic acid, m. p. 37—38°. The brucine salt, m. p. 135°, obtained from storax cinnamic acid is the hydrogen salt (compare Marckwald and Meth, Abstr., 1906, i, 880).

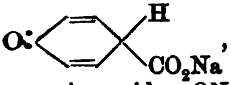
A new *cinnamic acid* has been isolated from synthetical cinnamic acid by crystallisation from 75% alcohol, evaporating the mother liquor and repeating this six times, the final mother liquor yields an acid which crystallises from light petroleum in triclinic needles, m. p. 127—128°. This is the eighth cinnamic acid obtained. W. R.

Chemical Process of Synthesis by Absorption of Carbon Dioxide. Karl Brunner (*Annalen*, 1907, **351**, 313—331).—In such reactions as Wanklyn's synthesis of sodium propionate (*Annalen*, 1858, **107**, 126), Kolbe and Lautermann's synthesis of salicylic acid (*Annalen*, 1860, **113**, 126), Kolbe's reduction of carbon dioxide to formic acid (*Annalen*, 1861, **119**, 251; Lieben, Abstr., 1895, ii, 348), Kekule's synthesis of benzoic acid from bromobenzene, sodium, and carbon dioxide (*Annalen*, 1866, **137**, 181), and Grignard's and Zelinsky's syntheses (Abstr., 1902, i, 675), which mostly consist of the union of carbon dioxide with a carbon atom of another molecule and take place only in presence of metals such as potassium or sodium, or of the interaction of carbon dioxide and organo-metallic compounds or similar reducing alkali compounds, the carbon dioxide must be considered as undergoing reduction, one of the double carbon oxygen linkings being opened,  $\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O}} \longrightarrow -\mathrm{C}{<}^{\mathrm{O}}_{\mathrm{O\cdot M''}}$. The formation of hydroxy-carboxylic acids from phenols is discussed from this point of view. The most convenient method of accomplishing this synthesis is to heat the phenol with glycerol, D 1·26, and potassium hydrogen carbonate in a current of carbon dioxide. Details are given of experiments with a number of phenols at different temperatures; under the most favourable conditions, the carboxylic or dicarboxylic acids are obtained in 40—50% yields. The following explanation is given of the synthesis of salicylic acid; the action of carbon dioxide on sodium phenoxide at the ordinary temperature results in the formation of the complexes $C_6H_5\cdot O\cdot$ and $\cdot CO\cdot ONa$, which combine to form sodium phenyl carbonate; this decomposes at 85° (Tijmstra, Abstr., 1905, i, 439), again forming sodium phenoxide and carbon dioxide. If the temperature is raised and the escape of carbon dioxide prevented, or if carbon dioxide is supplied in a continuous current, the group $\cdot CO_2Na$ combines with C_6H_5O, which acts in this case in the quinonoid form,



or 

, the resulting salt, 

or 

, being probably Tijmstra's supposed sodium *o*-carboxyphenoxide, $ONa\cdot C_6H_4\cdot CO_2H$; the final stage is the isomeric change into the *o*- or *p*-hydroxybenzoate. G. Y.

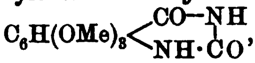
Preparation of Acetylsalicylamide KALLE & Co. (D.R.-P. 177054).—Acetylsalicylamide may be conveniently prepared and in good yield by mixing salicylamide (50 parts) with 30 parts of glacial acetic acid and 45 parts of acetic anhydride, and warming for five to six hours at 80—90°; on cooling, the product separates and is crystallised from chloroform. G. T. M.

Derivatives of 5-Aminosalicyclic Acid [5-Amino-2-hydroxybenzoic Acid]. ARNALDO PIUTTI (*Gazzetta*, 1906, **36**, ii, 734—738). [With FABRIZIO COBELLIS and DIEGO GANDOLFO.]—This preliminary communication merely gives the constitutions and m. p.'s of compounds obtained by the action of oxalic, malonic, succinic, citraconic, or phthalic acid on 5-amino-2-hydroxybenzoic acid or the corresponding aminomethoxybenzoic acid. These compounds are to be fully described later. T. H. P.

New Case of Wandering of an Alkyl Group. JACQUES POLLAK and J. GOLDSTEIN (*Annalen*, 1907, **351**, 161—171. Compare Goldschmiedt and Herzig, Abstr., 1882, 616; Heinisch, Abstr., 1894, i, 34, 527; Arnstein, *ibid.*, 527; Hübner, Abstr., 1895, i, 366; Malaguti, *Ann. Chim. Phys.*, [ii], **64**, 152).—With the object of determining the position assumed by the nitro-group introduced into methyl trimethylpyrogallolcarboxylate on nitration, the nitro-acid was heated in expectation that on loss of carbon dioxide one of the two possible nitrotrimethylpyrogallols would be formed (Will, Abstr., 1888, 1089; Einhorn, Cobliner, and Pfeiffer, Abstr., 1904, i, 238). The product, however, obtained on heating the acid under either the ordinary or reduced pressure, and distillation of the residue in a vacuum, contains neither of the nitrotrimethylpyrogallols, but consists of methyl nitrotrimethylpyrogallolcarboxylate and a small amount of nitropyrogallol dimethyl ether (Graebe, Abstr., 1887, 447; Heintz, *Jahresber.*, 1861, 448).

This wandering of a methyl group from a phenolic to a carboxylic hydroxyl is compared with a number of other similar cases. The lability of the alkyl group is considered to be determined by the presence of the electro-negative nitro-group (compare Salkowski and Rudolph, Abstr., 1878, 72).

The position of the nitro-group in nitrotrimethylpyrogallolcarboxylic acid is determined by reduction to the corresponding amine, which when fused with carbamide at 160—180° yields 2 : 4-*dioxy*-5 : 6 : 7-*trimethoxy*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,



$C_6H(OMe)_3<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, showing the nitro-group to be in the *o*-position to the carboxyl.

Methyl 2-nitrotrimethylpyrogallolcarboxylate, $NO_2\cdot C_6H(OMe)_3\cdot CO_2Me$, crystallises in colourless needles, m. p. 74°, and is insoluble in aqueous alkalis. The *acid*, $NO_2\cdot C_6H(OMe)_3\cdot CO_2H$, forms a colourless, crystalline mass, m. p. 154—155°.

Nitropyrogallol dimethyl ether, $NO_2\cdot C_6H_2(OMe)_2\cdot OH$, separates from alcohol in light yellow crystals, m. p. 112—114°, and dissolves in aqueous potassium hydroxide, forming an intense orange solution.

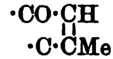
Methyl 2-aminotrimethylpyrogallolcarboxylate,

$$NH_2\cdot C_6H(OMe)_3\cdot CO_2Me,$$

m. p. 93—98°.

2:4-*Dioxy*-5:6:7-*trimethoxy*-1:2:3:4-*tetrahydroquinazoline* separates from alcohol in colourless crystals, m. p. 261—264° (decomp.), dissolves in aqueous alkalis, forming *alkali* derivatives, and when boiled with fuming hydriodic acid, yields a product, probably the *trihydroxydioxytetrahydroquinazoline*, crystallising in white needles, not melted at 300°. G. Y.

Santonic Acid. ANGELO ANGELI and LUIGI MARINO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 159—161).—As a means of ascertaining the constitution of santonin, the authors have attempted to study the products obtained on gradually breaking down the molecule in the manner successfully applied to the terpenes, more especially by Baeyer, Wagner, and Tiemann.

In the present preliminary communication, oxidation by permanganate is considered, and, as santonin is insoluble in water, santonic acid is employed. The oxidation products obtained, in addition to formic and oxalic acids, are: (1) an unstable, yellow, oily, dibasic *acid*, $C_{15}H_{20}O_7$, which reacts readily with hydroxylamine and hydrazines, reduces ammoniacal silver nitrate and Fehling's solutions, and yields iodoform on treatment with iodine and potassium hydroxide. From these reactions it may be regarded as possessing the formula $CO_2H\cdot C_{10}H_{14}(CO\cdot CO_2H)(COMe)\cdot OH$, and its formation is probably due to the oxidation of a group of the form  $\begin{matrix}\cdot CO\cdot CH \\ \quad\ \| \\ \cdot C\cdot CMe\end{matrix}$ to $\cdot CO\cdot CO_2H$ and $\cdot C\cdot COMe$. (2) A *tetracarboxylic acid*, $C_{11}H_{16}O_8$, m. p. about 165°, at which temperature it loses carbon dioxide and yields a product to be described later; its constitution may probably be represented by the scheme: $C_6H_{12}(CO_2H)_2\!:\!C(CO_2H)_2$.

The authors regard it as highly probable that santonic acid contains a bridge consisting of a methylene group situated in the ring containing the ketonic group. T. H. P.

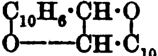
Benzaldehyde-*o*-aminophenylhydrazone. HARTWIG FRANZEN (*Ber.*, 1907, 40, 909—912).—This is the first examination of aminophenylhydrazones.

Benzaldehyde-o-aminophenylhydrazone, $CHPh\!:\!N\cdot NH\cdot C_6H_4\cdot NH_2$, obtained by the reduction of the corresponding *o*-nitrohydrazone in ammoniacal alcohol by sodium hyposulphite, crystallises in slender, yellow needles, m. p. 142°. The unstable *hydrochloride*,

$$C_{13}H_{13}N_3,HCl,$$

is colourless. When a suspension of the hydrazone in 2% hydrochloric acid is treated with a current of steam for five minutes, it is converted into the hydrochloride of 2-phenylbenziminazole (Pawlewski, Abstr., 1903, i, 661). An attempt to prepare an acetyl derivative also yielded phenyl benziminazole. W. R.

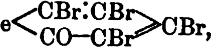
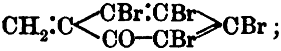
β-Hydroxynaphthaldehyde. II. Mario Betti and Curio M. Mundici (*Gazzetta*, 1906, **36**, ii, 655—660. Compare Abstr., 1905, i, 213).—The results already described (*loc. cit.*) show that although in many reactions β-hydroxynaphthaldehyde exhibits the normal behaviour of aromatic *o*-hydroxyaldehydes, yet some of the changes which it undergoes are characterised by the ease with which the aldehyde group tends to become detached from the naphthol nucleus. In the present paper are described the results obtained by reducing the hydroxyaldehyde in various ways. A series of compounds is obtained terminated by 1-methyl-β-naphthol (compare Fries and Hübner, Abstr., 1906, i, 190), which is the most completely reduced product.

Reduction of β-hydroxynaphthaldehyde by zinc and acetic acid yields: (1) *bisoxynaphthene-ethane*,  $\begin{matrix} C_{10}H_6\cdot CH\cdot O \\ O\text{———}CH\cdot C_{10}H_6 \end{matrix}$, which crystallises from benzene in colourless needles, m. p. 261—262°, gives a yellowish-red coloration with concentrated sulphuric acid and dissolves sparingly in acetic acid or alcohol. (2) A small quantity of *dinaphtholcarbinol*, $OH\cdot C_{10}H_6\cdot CH(OH)\cdot C_{10}H_6\cdot OH$, which crystallises from alcohol in lemon-yellow, thick needles or flattened prisms, m. p. 232°, dissolves in concentrated sulphuric acid giving a yellow coloration, gives a brown colour with ferric chloride in alcoholic solution, and is readily soluble in alkalis. (3) 1-Methyl-β-naphthol, which has the normal molecular weight in freezing acetic acid and dissolves in sulphuric acid giving a yellowish-red solution; it yields a *picrate*, m. p. 162—163°, and a *benzoyl* derivative, $C_{18}H_{14}O_2$, m. p. 115—116°.

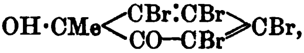
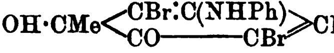
A better yield of dinaphtholcarbinol is obtained if the reduction of the β-hydroxynaphthaldehyde is affected by means of aluminium in alkaline solution.

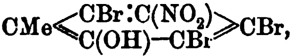
Reduction with aluminium amalgam gives rise to: (1) dinaphtholmethane, $CH_2(C_{10}H_6\cdot OH)_2$; (2) *1-hydroxymethyl-$\beta$-naphthol*, (*hydroxynaphthoic alcohol*), $OH\cdot C_{10}H_6\cdot CH_2\cdot OH$, which crystallises from chloroform in shining, white needles, m. p. 188—189° (decomp.), dissolves in concentrated sulphuric acid giving a reddish-yellow coloration, is soluble in alcohol or benzene, and in alcoholic solution yields a bluish-green coloration with ferric chloride.

T. H. P.

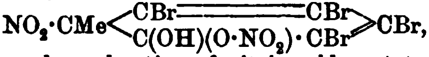
Action of Nitric Acid on Halogen Derivatives of *o*-Alkylphenols. Theodor Zincke and W. Klostermann (*Ber.*, 1907, **40**, 679—685. Compare Abstr., 1905, i, 879, 882).—Tribromo-*p*-toluquinone is formed by the vigorous action of concentrated nitric acid (D 1·48—1·5) on tetrabromo-*o*-cresol. If the action of the nitric acid is conducted in the cold, or in the presence of glacial acetic acid, *tetrabromo-o-methylquinnitrole*,  $NO_2\cdot CMe{<}\begin{matrix} CBr{:}CBr \\ CO{-}CBr \end{matrix}{>}CBr$, is formed as a sulphur-yellow, crystalline powder, which softens at 71° and decomposes at higher temperatures. When acted on by moist ether or by methyl alcohol, it forms *tetrabromo-o-methylenequinone* (*tetrabromo*-o-*quinonemethide*),  $CH_2{:}C\left\langle\begin{matrix}CBr{:}CBr\\CO{-}CBr\end{matrix}\right\rangle CBr$; this separates from ether in yellow, glistening leaflets and from methyl alcohol as a sulphur-yellow, granular powder, m. p. about 130°.

Tetrabromo-*o*-methylquinnitrole is converted on reduction into tetrabromo-*o*-cresol.

Tetrabromo-o-*methylquinol*,  $OH{\cdot}CMe\left\langle\begin{matrix}CBr{:}CBr\\CO{-}CBr\end{matrix}\right\rangle CBr$, prepared by boiling tetrabromo-*o*-methylquinnitrole with light petroleum or with benzene, separates from a mixture of light petroleum and benzene in glistening, yellow needles, m. p. 135—136°. When warmed with glacial acetic acid and a little sulphuric acid, it evolves hydrogen bromide and is converted into tribromo-*p*-toluquinone; when reduced by stannous chloride, it forms tetrabromo-*o*-cresol. Its *acetyl* derivative separates from benzene or glacial acetic acid in yellow leaflets, m. p. 110°. Its *anilide*,  $OH{\cdot}CMe\left\langle\begin{matrix}CBr{:}C(NHPh)\\CO{-\!-\!-}CBr\end{matrix}\right\rangle CBr$, separates from a mixture of light petroleum and benzene in glistening leaflets, m. p. 160—161°.

3 : 4 : 6-*Tribromo*-5-*nitro*-o-*cresol*,  $CMe\left\langle\begin{matrix}CBr{:}C(NO_2)\\C(OH){-}CBr\end{matrix}\right\rangle CBr$, obtained by the action of alcoholic sodium hydroxide on tetrabromo-*o*-methylquinnitrole, forms colourless needles, m. p. 177° (decomp.). When reduced by tin and hydrochloric acid, it forms 3 : 4 : 6-tribromo-5-amino-*o*-cresol. When oxidised by ferric chloride, it forms 3 : 4 : 6-tribromo-*p*-toluquinone.

Tetrabromo-o-*methylquinnitrole nitrate*,



$$NO_2{\cdot}CMe\left\langle\begin{matrix}CBr{=\!=\!=\!=}CBr\\C(OH)(O{\cdot}NO_2){\cdot}CBr\end{matrix}\right\rangle CBr,$$

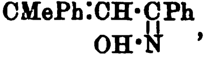
obtained by the prolonged action of nitric acid on tetrabromo-*o*-cresol, separates from a mixture of light petroleum and benzene in colourless needles, m. p. 99°, decomposing with evolution of a red gas.

The *compound*, $C_7H_4O_6N_2Br_4$ (possibly
$NO_2{\cdot}CHMe{\cdot}CBr{:}CBr{\cdot}CBr{:}CBr{\cdot}CO_2{\cdot}NO_2$),
obtained either by the action of sodium carbonate on the preceding compound or by the prolonged action of nitric acid on a solution of tetrabromo-*o*-cresol in glacial acetic acid, forms colourless needles, m. p. 139° (decomp.). It reacts vigorously with alkalis and with aniline.

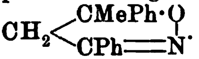
A. McK.

Preparation of Ketones from Aldehydes by Means of Diazomethane. Hans Meyer (*Ber.*, 1907, **40**, 847—848. Compare Abstr., 1905, i, 87).—The products formed by the action of diazomethane on *m*- and *p*-nitrobenzaldehydes and thought to be possibly enolic compounds, are now found to be identical with the nitroacetophenones, which when pure are colourless, give red colorations with alcoholic alkalis, and are soluble in boiling aqueous alkalis. Contrary to Schlotterbeck's statement (this vol., i, 185) that the reactivity of diazomethane with aldehydes decreases with increasing molecular weight of the latter, the nitrobenzaldehydes enter into the reaction more energetically than does benzaldehyde.

G. Y.

Stereoisomeric Oximes of Dypnone and Benzylideneacetophenone. FERDINAND HENRICH [and, in part, RAAB and RUPPENTHAL] (*Annalen*, 1907, 351, 172—185. Compare Abstr., 1904, i, 431, 751).—The chemical properties of the subtance, m. p. 78°, formed by the action of concentrated sulphuric acid on *syn*-dypnone-oxime and previously assumed to be the *anti*-oxime, 

$$\begin{array}{l}\mathrm{CMePh{:}CH\cdot CPh}\\ \qquad\quad\mathrm{OH\cdot N}\end{array}$$

, appeared to agree better with the isomeric *iso*oxazoline structure, 

$$\mathrm{CH_2}<\begin{array}{l}\mathrm{CMePh\cdot O}\\ \mathrm{CPh{=\!=}N}\end{array}$$

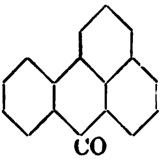
. The present work was undertaken with the object of deciding between these constitutions. As reduction of both dypnone-oximes, with sodium amalgam in acetic acid solution or with sodium and alcohol, leads to the formation of *aγ-diphenylbutylamine*, whilst the reduction product of the *iso*oxazoline would be the hydroxyamine, $OH\cdot CMePh\cdot CH_2\cdot CHPh\cdot NH_2$, the author decides in favour of the *anti*-oxime formula. The oximes of benzylideneacetophenone also have been examined and compared with those of dypnone.

aγ-Diphenylbutylamine hydrochloride, $C_{16}H_{19}N,HCl$, crystallises in needles, m. p. 226—228°; the *platinichloride* forms yellow needles, m. p. 195°; the *aurichloride* and *picrate*, m. p. 187°, are obtained as yellow precipitates; the *mercurichloride* forms white needles; the *a-tartrate*, $C_{16}H_{19}N,C_4H_6O_6$, crystallises in white needles, m. p. 234°, and yields the inactive *base*.

anti-Benzylideneacetophenoneoxime, formed from the ketone and hydroxylamine in alkaline alcoholic solution, crystallises in white needles, m. p. 75° (compare Goldschmidt, Abstr., 1895, i, 422; Claus, Abstr., 1897, i, 189), does not undergo the Beckmann transformation, and on reduction with sodium and alcohol yields *aγ-diphenylpropylamine*. The *hydrochloride*, $CH_2Ph\cdot CH_2\cdot CHPh\cdot NH_2,HCl$, crystallises in colourless needles, m. p. 195°; the *picrate*, $C_{15}H_{17}N,C_6H_2(NO_2)_3\cdot OH$, long needles or leaflets, m. p. 155°; the *platinichloride*, $(C_{15}H_{17}N)_2,H_2PtCl_6$, was analysed; the *d-tartrate*, $C_{15}H_{17}N,C_4H_6O_6$, forms white needles, m. p. 168°, and yields the inactive base.

syn-Benzylideneacetophenoneoxime, formed in alcoholic hydrochloric acid solution, separates as a crystalline mass, m. p. 115—116°, is reduced by sodium and alcohol, forming aγ-diphenylpropylamine, and is converted by hot concentrated sulphuric acid into the *anti*-oxime, from which it differs in forming a crystalline *hydrochloride*. The *phenylurethane*, $C_{22}H_{18}O_2N_2$, crystallises in white needles, m. p. 165°. The *acetyl* derivative of the *syn*-oxime, $C_{17}H_{15}O_2N$, forms white crystals, m. p. 135°. When treated with phosphorus pentachloride in ethereal solution, the *syn*-oxime undergoes Beckmann's transformation, forming cinnamoylanilide, m. p. 153°, which is formed also by Werner and Piquet's method (Abstr., 1905, i, 66). G. Y.

Preparation of Benzanthrone and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 176018 and 176019. Compare Abstr., 1906, i, 888).—It was formerly shown that certain aminoanthraquinones condense with glycerol so as to form compounds containing two new rings, and it has now been discovered that anthraquinone and its sulphonic acids and anthranol and hydroxyanthranol also condense with this reagent to form a new series of ketones, the *benzanthrones*, the compounds from the aminoanthraquinones being called *benzanthronequinolines*. *Benzanthrone* is obtained by heating a mixture of anthranol, glycerol, and concentrated sulphuric acid at 120°, a vigorous action sets in and sulphur dioxide is evolved; the product crystallises from alcohol in pale yellow needles, m. p. 170°. This compound may also be prepared from anthraquinone and other condensing agents such as zinc chloride, concentrated hydrochloric acid and aniline sulphate may be employed. Benzanthrone-β-sulphonic acid can be produced similarly from the corresponding sulphonic acid of anthraquinone or anthranol. Benzanthrone may even be obtained by condensing anthracene itself with glycerol and concentrated sulphuric acid.



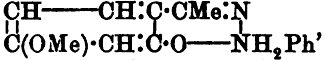
G. T. M.

Hydrazones of Aromatic Hydroxy-ketones. Alkali-insoluble Phenols. HENRY A. TORREY and H. B. KIPPER (*J. Amer. Chem. Soc.*, 1907, **29**, 77—81).—A study has been made of the action of phenylhydrazine on hydroxyacetophenones and hydroxybenzophenones. It was thought that, under certain conditions, not only would the keto-group be attacked, but that possibly the hydroxyl group might react with the hydrogen of the imino-group with the formation of a five-membered ring by a condensation similar to that occurring between phenylhydrazine and ethyl acetoacetate. Although a condensation of this kind did not take place, the character of the hydroxyl group was affected, the hydrazones formed being insoluble in alkali hydroxides. Phenolic compounds which are insoluble in alkali hydroxides have been described previously by Anselmino (Abstr., 1903, i, 121) and by Rogoff (Abstr., 1905, i, 883).

The phenylhydrazone of resacetophenone is soluble in alkali hydroxides, but that of its methyl ether, paeonol,

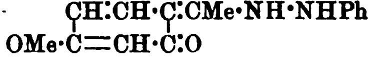
$$OMe\cdot C_6H_3(OH)\cdot CMe{:}N\cdot NHPh,$$

in which the only free hydroxyl group is in the *o*-position to the keto-side-chain, is insoluble. The insolubility of the latter hydrazone suggests either that the hydroxyl group has formed with the imino-group a six-membered ring,



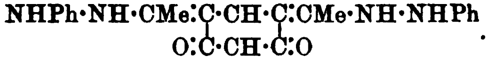
$$\begin{array}{l} CH\text{——}CH{:}C\cdot CMe{:}N \\ \| \qquad\qquad\quad | \qquad\qquad\quad | \\ C(OMe)\cdot CH{:}C\cdot O\text{——}NH_2Ph \end{array}$$

, or that the hydrogen is so feebly acid that the alkali salt, if formed, suffers immediate hydrolysis. Resodiacetophenone (2 : 4-dihydroxy-1 : 5-diacetophenone) yields a *bisphenylhydrazone*, m. p. 291°, which, as would be expected, is insoluble in alkali hydroxides. These compounds, however, which do not dissolve in aqueous alkali hydroxides are soluble in potassium ethoxide, but, on adding water, the original compound is precipitated. Another possible explanation of the insolubility of these hydrazones is that they have a quinonoid structure and thus do not contain a hydroxyl group; in this case paeonolphenylhydrazone and resodiacetophenonebisphenylhydrazone would be represented respectively by the formulæ



$$\begin{array}{l}\mathrm{\quad\; CH{:}CH{\cdot}C{:}CMe{\cdot}NH{\cdot}NHPh}\\ \mathrm{OMe{\cdot}C{=\!=}CH{\cdot}C{:}O}\end{array}$$

and



$$\begin{array}{c}\mathrm{NHPh{\cdot}NH{\cdot}CMe{:}C{\cdot}CH{\cdot}C{:}CMe{\cdot}NH{\cdot}NHPh}\\ \mathrm{O{:}C{\cdot}CH{\cdot}C{:}O}\end{array}$$

Dibenzoylresacetophenonephenylhydrazone,

$$C_6H_3(OBz)_2{\cdot}CMe{:}N{\cdot}NHPh,$$

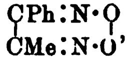
m. p. 183°, can be obtained either by the action of phenylhydrazine on dibenzoylresacetophenone or by that of benzoyl chloride on a solution of resacetophenonephenylhydrazone in alkali hydroxide. *Dibenzoylresacetophenone* crystallises from alcohol and is insoluble in water. 1 : 4-Dihydroxyphenylene diphenyl diketone *bisphenylhydrazone*, m. p. 172—174°, forms yellow crystals and is insoluble in alkali hydroxides. 1 : 3-Dihydroxyphenylene diphenyldiketone *bisphenylhydrazone*, m. p. 292—293°, is a white, crystalline substance insoluble in alkali hydroxides. E. G.

α-Diketones from α-Ketoaldoximes; a New Synthesis with Diazo-compounds. Wilhelm Borsche (*Ber.*, 1907, **40**, 737—744).—Although aldehyde-arylhydrazones are easily coupled with aromatic diazo-compounds to form formazyl compounds, this reaction does not succeed with aldoximes. In oximes, such as methylglyoxalmonoxime, in which the ·CH:N·OH group is situated immediately next to a carbonyl group the hydrogen atom is more reactive and can be replaced by the diazo-group. Such compounds lose nitrogen and yield monoximes of aliphatic aromatic diketones,

$$CH_3{\cdot}CO{\cdot}CH{:}N{\cdot}OH \longrightarrow CH_3{\cdot}CO{\cdot}C({:}N{\cdot}OH){\cdot}N_2Ar$$
$$\longrightarrow CH_3{\cdot}CO{\cdot}C({:}N{\cdot}OH){\cdot}Ar,$$

from which the diketones themselves are obtained on heating with dilute sulphuric acid. This at present forms the easiest method of preparing such diketones.

Attempts to carry through the same reaction with *iso*nitrosoacetophenone and so to obtain benzil and its homologues were less successful.

β-Keto-α-oximino-α-phenylpropane, OH·N:CPh·COMe, is obtained from *iso*nitroso-acetone and diazobenzene chloride in faintly yellow plates, m. p. 166—167°, identical with the compound prepared by Kolb (Abstr., 1896, i, 576). Heated with excess of hydroxylamine hydrochloride, it forms the acetylbenzoyldioxime, m. p. 231—233°, OH·N:CPh·CMe:N·OH, described by von Pechmann and Müller (Abstr., 1888, 1087). On oxidation with potassium ferricyanide in alkaline solution, *phenylmethylglyoxime peroxide*,  $\begin{array}{l}\mathrm{CPh{:}N{\cdot}O}\\ \mathrm{CMe{:}N{\cdot}O}\end{array}$, is formed, crystallising in colourless needles, m. p. 95°.

Acetylbenzoyl, obtained by warming the oxime with dilute sulphuric acid, is a dark yellow oil, volatile in steam, and possessing a characteristic sweet and quinone-like odour (compare Kolb, *loc. cit.*).

*β-Keto-α-oximino-α-*p*-tolylpropane*, $CH_3{\cdot}C_6H_4{\cdot}C({:}N{\cdot}OH){\cdot}CO{\cdot}CH_3$, forms large, colourless, rhombic plates, m.p. 161—162°; the corresponding *dioxime* crystallises in colourless needles, m.p. above 230° (decomp.).

β-Keto-a-oximino-2 : 4-dimethylphenylpropane,

$$C_6H_3Me_2\cdot C(:N\cdot OH)\cdot CO\cdot CH_3,$$

is obtained as colourless, microscopic needles, m. p. 141—142°.

β-Keto-a-oximino-a-o-methoxyphenylpropane,

$$OMe\cdot C_6H_4\cdot C(:N\cdot OH)\cdot CO\cdot CH_3,$$

crystallises in long needles, m. p. 131—132°.

*β-Keto-a-oximino-a-*p*-methoxyphenylpropane*,

$$OMe\cdot C_6H_4\cdot C(:N\cdot OH)\cdot CO\cdot CH_3,$$

crystallises in short, thick needles, m. p. 152—153°. It forms acetyl-*p*-anisoyl-*amphi*dioxime, m. p. 215°, whilst when heated with dilute sulphuric acid, *acetyl*-p-*anisoyl*, $OMe\cdot C_6H_4\cdot CO\cdot CO\cdot CH_3$, is formed, crystallising in long, citron-yellow needles, m. p. 48°. About half of the oxime is converted in this manner, the rest undergoing a Beckmann rearrangement and yielding pyruvic *p*-anisidide,

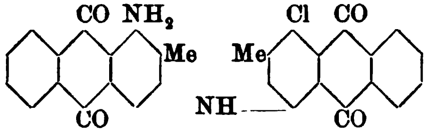
$$OMe\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot CH_3,$$

crystallising in colourless, minute needles, m. p. 129—130°. The magnitude of the rearrangement is to be attributed to the influence of the *p*-methyl group (compare Werner, Abstr., 1906, i, 180).

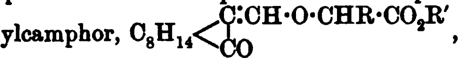
By the interaction of *iso*nitrosoacetophenone and diazobenzene salts, *a*-benzilmonoxime was obtained. E. F. A.

Preparation of Halogen Derivatives of β-Hydroxyanthraquinone. R. WEDEKIND & Co. (D.R.-P. 175663).—The β-hydroxyanthraquinones readily undergo bromination when suspended in water, giving rise to di- and tri-bromo-derivatives. *Dibromo*-2-*hydroxyanthraquinone*, $C_{14}H_6O_3Br_2$, is produced by adding bromine to a suspension of 2-hydroxyanthraquinone in water acidified with sulphuric acid. Anthraflavic acid yields either di- or tri-bromo-anthraflavic acid, depending on the amount of bromine employed. Flavopurpurin behaves in a similar manner. G. T. M.

[Preparation of Dianthraquinonylamine Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 176956).—4-Chloro-1-amino-2-methylanthraquinone when dissolved in concentrated sulphuric acid and treated with nitrating acid containing 20—21% HNO_3 becomes converted into a substance having the composition $C_{30}H_{19}O_4N_2Cl$, which is probably a dianthraquinonylamine having the annexed constitution: other substituted 1-amino-anthraquinones containing a halogen in position 4 and some other substituent in position 3 undergo this condensation and give rise to analogous di-anthraquinonylamines. When these compounds are condensed with phenols or aromatic amines, blue colouring matters are produced, which dye unmordanted wool in various shades of blue which are characterised by their fastness to light and scouring agents. G. T. M.



Camphoformyl-acetic and -*a*-Propionic Esters. CHARLES WEIMANN (*Ann. Chim. Phys.*, 1907, [viii], 10, 378—394).—Haller and Couréménos (Abstr., 1905, i, 523) have shown that two optical isomerides are formed by the introduction of the cyanocamphor group into propionic acid in the α-position. In the present paper, derivatives of formylcamphor,



$C_8H_{14}\left<\begin{matrix}C{:}CH\cdot O\cdot CHR\cdot CO_2R' \\ | \\ CO\end{matrix}\right.$, prepared by the action of sodioformylcamphor (Bishop, Claisen, and Sinclair, Abstr., 1895, i, 62) on bromoacetic and α-bromopropionic esters in boiling toluene solution, are described, the chief object of the work being to produce evidence as to how far it may be considered to be a general rule that the union of an active molecule with the asymmetric carbon atom of a racemic compound results in the formation of two optical isomerides.

Ethyl camphoformylacetate, R = H, R′ = Et, separates from light petroleum in white crystals, m. p. 56°, b. p. 190—210°/20 mm., $[\alpha]_D$ + 148°15·65′, and is hydrolysed readily at the ordinary temperature by aqueous alkali carbonates, forming sodioformylcamphor and sodium glycollate, by water under pressure at 150°, yielding formylcamphor, glycollic acid, and ethyl alcohol, or by cold hydrochloric acid, in consequence of which it gives gradually with ferric chloride the violet coloration characteristic of formyl camphor.

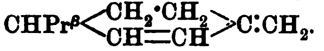
Methyl camphoformylacetate, R = H, R′ = Me, separates from light petroleum in white crystals, m. p. 91°, b. p. 215/23 mm., $[\alpha]_D$ + 156°32·72′, and gives reactions similar to those of the ethyl ester.

Methyl camphoformyl-α-propionate, R = Me, R′ = Me, separates from methyl alcohol in large, white crystals, m. p. 71·5°, b. p. 195—205°/20 mm., $[\alpha]_D$ + 148°10·92′, and undergoes hydrolysis in the same manner as the camphoformylacetates, yielding formylcamphor, lactic acid, and methyl alcohol; no trace of an optical isomeride could be found on fractional crystallisation from light petroleum.

Ethyl camphoformyl-α-propionate, R = Me, R′ = Et, is obtained as a yellow oil, b. p. 205—215°/20 mm., D^0 1·078, $[\alpha]_D$ + 122°34′.

From the identity of the molecular rotations of methyl camphoformylacetate and methyl camphoformyl-α-propionate and of the specific rotations of methyl camphoformyl-α-propionate and ethyl camphoformylacetate, it is concluded that the camphoformylpropionates are racemic compounds. G. Y.

Preparation of Pinene Hydrochloride. CHEMISCHE FABRIK UERDINGEN LIENAU & Co. (D.R.-P. 175662).—Pinene hydrochloride as usually prepared does not keep unless it has been repeatedly crystallised from alcohol or purified in some other costly manner. It is now found that a stable form of the substance can be cheaply and readily prepared by treating the crude material with hydrolytic agents until the "saponification number" of the product is equal to that of the highly purified compound. This is best carried out by heating the hydrochloride with the calculated amount of an alkali hydroxide in dilute aqueous solution. A further purification is effected by warming the hydrochloride with sulphuric acid, D 1·5, at 80° to 100°; this operation removes an oily impurity which lowers the melting point of the hydrochloride. Phosphoric acid may be substituted for sulphuric acid, and the pinene hydrochloride is distilled off in steam and further purified by distillation or sublimation. G. T. M.

Synthetical and Natural Phellandrenes. Iwan L. Kondakoff and Iwan Schindelmeiser (*J. pr. Chem.*, 1907, [ii], **75**, 141—145. Compare Abstr., 1903, i, 845; 1905, i, 801).—Synthetical phellandrene from carvomenthene dibromide resembles the natural hydrocarbon except in its b. p. and molecular rotation. It forms two nitroso-derivatives crystallising in stellate clusters, m. p. 102—103·5°, sparingly soluble in benzene, and in thin needles, m. p. 94—95°, which are more readily soluble; these resemble the α- and β-nitroso-derivatives of ψ-phellandrene. The synthetical phellandrene is represented by the formula 

$$CHPr^{\beta}<\begin{matrix}CH_2\cdot CH_2\\ CH{=}CH\end{matrix}>C{:}CH_2.$$

The action of hydrogen chloride on β-phellandrene in glacial acetic acid solution leads to the formation of a monohydrochloride, m. p. 126°, and an *i-trans*dipentene dihydrochloride, m. p. 50°, b. p. 122·5—125°/16 mm. On treatment with alcoholic potassium hydroxide, the mixture of hydrochlorides obtained from ψ-phellandrene yields dipentene and a monochloro-compound. The bearing of these changes on the constitution of natural phellandrene and of thujene is discussed (compare Semmler, this vol., i, 145). G. Y.

Constitution of Terpinene, Origanol, Sabinene, Dipentene, and their Derivatives. Friedrich W. Semmler (*Ber.*, 1907, **40**, 751—757; this vol., i, 145).—Polemical. A reply to Wallach (this vol., i, 229). E. F. A.

Presence of β-Phenylethyl Alcohol in the Essence of Pine-needles of Aleppo, Algeria. Émilien Grimal (*Compt. rend.*, 1907, **144**, 434—435).—From the essential oil of pine-needles from Aleppo, Algeria, the author has isolated phenylethyl alcohol, hitherto detected only in the essential oils of neroli and of roses. E. H.

Autoxidation of Colophony. Wilhelm Fahrion (*Zeitsch. angew. Chem.*, 1907, **20**, 356—361. Compare Abstr., 1902, i, 165; 1904, i, 332)—Doubt having been cast on the author's earlier statements by Tschirch and Studer (Abstr., 1904, i, 79), the work has been repeated and verified. The compound, $C_{20}H_{80}O_2$, previously called sylvic acid is identical with abietic acid the formula, $C_{19}H_{28}O_2$, assigned to the latter by Mach being incorrect; the compound first formed by autoxidation is dioxyabietic acid, $C_{20}H_{80}O_4$, which finally passes into tetraoxyabietic acid, $C_{20}H_{80}O_6$. Dioxyabietic acid loses water when heated at 120°, also when treated with alcohol, alcoholic sulphuric acid, or an aqueous solution of sodium chloride. The anhydro-acids formed have not been isolated in a pure state, the portion soluble in light petroleum being called *a-anhydrodioxyabietic acid*, the insoluble portion, *β-anhydrodioxyabietic acid*. These substances are also present in colophony which has been exposed in the powdered state for some time to the air. W. H. G.

Glucoside Hydrolysed by Emulsin: Bakankosin from the Seeds of a Madagascar Strychnos. EMILÉ BOURQUELOT and HENRI HERISSEY (*Compt. rend.*, 1907, **144**, 575—577).—Laurent (*J. Pharm. Chim.*, 1907, [vi], **25**, 225) by the application of Bourquelot's method (Abstr., 1902, ii, 55) has ascertained that glucosides occur in the seeds of *Strychnos nux vomica, S. Ignatii,* and *S. bakanko* (? *S. vacacoua*). From the last-mentioned the authors by extracting the oil-free seeds with alcohol have obtained *bakankosin,* which forms large, colourless crystals, m. p. 157°, and remelts at about 200°, has $[\alpha]_D$ −205·2°. The glucoside contains nitrogen and is hydrolysed by boiling dilute mineral acids and slowly by emulsin, furnishing dextrose. Neither bakankosin nor its hydrolytic products are toxic. T. A. H.

New Rhamnoside from Ipomœa Turpethum. EMIL VOTOČEK and J. KASTNER (*Zeitsch. Zuckerind. Böhm.*, 1907, **31**, 307—316).—Roots of *Ipomœa Turpethum* (the drug *radix turpethi*) contains, in addition to turpethin (Spirgatis, *Annalen,* **139**, 41; and Kromer, Abstr., 1893, i, 482), two other glucosides, α-turpethein and in smaller quantity, β-turpethein.

α-Turpethein is readily soluble in light petroleum. When heated with barium hydroxide, the *barium* salt of *α-turpetheic acid* is obtained as a light yellowish-brown, amorphous mass readily soluble in water, m. p. 185°. The free acid when hydrolysed with 10% sulphuric acid yields a non-volatile hydroxy-acid, $C_{16}H_{32}O_3$, isomeric or identical with jalapic, ipomeolic and tampicolic acids; a volatile fatty acids, probably one of the valeric acids, and rhamnose.

β-Turpethein is obtained as a yellow powder insoluble in light petroleum. When β-turpetheic acid is hydrolysed, rhodeose, dextrose, a non-volatile higher fatty acid, and volatile fatty acids are obtained. N. H. J. M.

Grasshopper-Green not Chlorophyll. HANS PRZIBRAM (*Annalen,* 1907, **351**, 44—51).—Spectroscopic examination having failed to decide the question of the identity of the colouring matter obtained from grasshoppers (*Locusta, Orphania, Mantis, Bacillus, &c.*) with chlorophyll, the author has investigated these substances chemically and now describes experiments which show that they are different.

The ethereal extract of grasshopper-green remains unchanged in the dark, but is bleached on exposure to light; when boiled with alcoholic potassium hydroxide, it becomes turbid and wine yellow, and on repeated boiling with fresh quantities of the alkali, deposits a yellow *precipitate.* A chlorophyll solution treated in the same manner becomes a deep green and yields a *substance* separating in black drops.

On addition of concentrated sulphuric acid, the grasshopper-green solution becomes a turbid yellow and after some time reddish-brown, whilst chlorophyll forms a clear, deep bluish-green solution gradually resuming its original yellowish-green colour.

The action of fuming nitric acid on grasshopper-green leads to the formation of a colourless, opalescent *liquid,* and of a whitish-green *precipitate,* but on chlorophyll to the formation of a turbid, yellow solution, gradually becoming transparent. G. Y.

Constitution of Tannin. II. Maximilian Nierenstein (*Ber.*, 1907, **40**, 916—918. Compare Abstr., 1905, i, 914).—The acetyl product, m. p. 129°, obtained from tannin is a mixture of two penta-acetyltannins and not a hexa-acetyl derivative; Dekker's phthalic anhydride formula for tannin contains seven hydroxyl groups and would be expected to yield a hepta-derivative (Abstr., 1906, i, 686, 974). One of the *penta-acetyltannins*, $C_{14}H_6O_9Ac_5$, m. p. 203—206°, gives, on oxidation with potassium persulphate in acetic acid, ellagic acid, and on hydrolysis with dilute sulphuric acid, gallic acid; the other has m. p. 166°. W. R.

Cannabinol, the Active Constituent of Hashish. Max Czerkis (*Annalen*, 1907, **351**, 467—472).—On fractional distillation of the light petroleum extract of hashish, Fränkel (*Arch. exp. Path. Pharm.*, 1903, **49**, 266) obtained a substance, cannabinol, $C_{21}H_{30}O_2$, b. p. 215°/0·5 mm., and found it to contain a phenolic hydroxyl and to form a trinitro-derivative. He considered, but could not prove, the second oxygen atom to be aldehydic. The author has undertaken the study of the constitution of cannabinol and gives an account of the few results so far obtained.

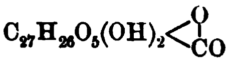
Cannabinol, b. p. 230°/0·1 mm. (corr.), on treatment with concentrated nitric acid in boiling glacial acetic acid solution, yields a *trinitroacetoxydicarboxylic acid*, $OAc\cdot C_{19}H_{24}(NO_2)_3(CO_2H)_2$, which is obtained as an amorphous, orange-yellow powder. The formation of the two carboxyl groups are ascribed to the oxidation of an aldehyde group and of a nucleus methyl, hence cannabinol may be represented by the formula, $OH\cdot C_{19}H_{25}Me\cdot CHO$. Oxidation by means of concentrated nitric acid in absence of a solvent leads to the formation of butyric and oxalic acids. On distillation with zinc dust, cannabinol yields a fluorescent oil, boiling at high temperatures. The results obtained suggest that the cannabinol is split into two complexes, $C_{13}H_{18}O$ and $C_8H_{12}O$; this requires further investigation. G. Y.

Preparation of a Soluble, Crystalline, Nitrogenous Constituent of Ergot (Secale cornutum). Ernst Vahlen (D.R.-P. 175590 and 175591).—See Abstr., 1906, i, 876. G. T. M.

Columbin. I. Th. Ulrich (*Annalen*, 1907, **351**, 363—371. Compare Hilger, Abstr., 1896, i, 623).—The investigation of columbin was undertaken as neither the formula nor the molecular weight of this substance had been determined with certainty by previous authors.

Columba root contains berberine and columbin, but contrary to the statements of previous authors, not columbic acid, which is formed when the only partially extracted root is treated with an aqueous alkali. The analytical results and molecular weight determination by the boiling point method show columbin to have the formula $C_{28}H_{30}O_9$, and to contain neither methoxy nor acetyl groups. It crystallises in rhombic needles, which are biaxial and show negative double refraction. G. Y.

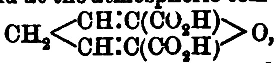
Columbin. II. Otto Frey (*Annalen*, 1907 **351**, 372—378. Compare preceding abstract).—The partially structural formula,

 $C_{27}H_{26}O_5(OH)_2<\begin{matrix}O\\ |\\ CO\end{matrix}$, is ascribed to columbin, since, contrary to Hilger's statement (Abstr., 1896, i, 623), when boiled with acetic anhydride and sodium acetate, it yields a *diacetyl* derivative, $C_{28}H_{28}O_9Ac_2$, crystallising in white needles, m. p. 218°, and, when boiled with potassium hydroxide and a small amount of water in a current of hydrogen, forms columbic acid, $OH\cdot C_{27}H_{30}O_7\cdot CO_2H$, crystallising in rosettes, m. p. 220°. Columbin contains four ethylene linkings, as it forms an *additive* compound with 4 mols. of bromine in chloroform solution. The *product* obtained on heating columbin with dilute hydrochloric acid in a sealed tube at 160°, probably contains acetone, as it gives the iodoform reaction and is coloured a weak red by sodium nitroprusside and sodium hydroxide. G. Y.

Picrotoxin. FRANCESCO ANGELICO (*Gazzetta*, 1906, **36**, ii, 645—654).—The author's researches deal with the isolation of picrotoxinin and picrotin from picrotoxin by treatment with either barium hydroxide or bromine (compare Meyer and Bruger, Abstr., 1899, i, 226) and with various derivatives obtained on oxidation.

Bromopicrotoxinin, which separates from solution when picrotoxin is suspended in boiling water and treated with bromine water, is readily oxidised by potassium permanganate in faintly alkaline solutions, yielding: (1) a small proportion of a white compound; (2) mainly a bromo-acid, which crystallises from water in white needles, m. p. 248—250° (decomp.), and may be identical with the acid obtained by Meyer and Bruger (*loc. cit.*) by decomposing bromopicrotoxinin dissolved in sodium hydroxide solution by means of acid. Its ethyl ester has m. p. 170° (decomp.). The acid is not attacked by potassium permanganate or dilute acids and does not reduce Fehling's solution. Oxidation with chromic acid in presence of dilute sulphuric acid oxidises it to another bromo-acid which crystallises from water in large, shining needles, decomposing at 170—180° and is sparingly soluble in water; this acid, when reduced by means of zinc and acetic acid, or boiled with alkali, or heated at its decomposition temperature, gives rise to products which react with phenylhydrazine.

Oxidation of picrotin by permanganate in a faintly acid solution yields: (1) a *compound*, $C_{15}H_{18}O_8$ or $C_{13}H_{18}O_7$, crystallising from acetic acid in nacreous leaflets, m. p. 254—255°; (2) a *compound* separating from acetic acid in small, mammillary crystals, m. p. about 245°. T. H. P.

The Pyran Series. VI. 4-Pyran-2:6-dicarboxylic Acids. EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. Chim.*, 1907, [iv], 1, 129—146. Compare Abstr., 1904, i, 762; 1906, i, 300; this vol., i, 147, 148, 181).—The *aε*-diketopimelic acids already described are converted by treatment with excess of sulphuric acid at the atmospheric temperature into 4-pyran-2:6-dicarboxylic acid,  $CH_2<\begin{matrix}CH:C(CO_2H)\\ CH:C(CO_2H)\end{matrix}>O$, which yields characteristic copper salts, usually containing water of crystallisation, which are stable at 100°, furnish unstable acid dichlorides, and cannot be transformed into the corresponding pyrans or the related pyridine or pyrone derivatives. Similarly, they do not form additive compounds of the types described by Fosse (Abstr., 1903, i, 357; 1905, i, 607), but yield unstable dibromides, the two atoms of bromine being attached to the cyclic oxygen.

4-*Pyran*-2 : 6-*dicarboxylic acid*, obtained by the general method, crystallises from boiling water in long, colourless needles, and is infusible without decomposition. The *methyl* ester, m. p. 121°, crystallises from dilute alcohol; the *ethyl* ester, m. p. 37°, separates in crystals from a mixture of ether and light petroleum. On treatment with phosphorus pentachloride, the acid yields the *dichloride*, m. p. 112°, which crystallises from benzene and, when dissolved in ammonia solution, yields the corresponding *diamide*, m. p. about 250°, which is crystalline and insoluble in most organic solvents. The *dianilide*, similarly obtained, m. p. 255°, crystallises from hot formic acid. Pyran-2 : 6-dicarboxylic acid is not hydrolysed by boiling water, but is readily attacked by alkalis. When boiled with an aqueous solution of mercuric chloride it is completely hydrolysed to the corresponding $\alpha\epsilon$-diketopimelic acid. It is assumed that in this reaction a molecule of mercuric chloride becomes attached to the cyclic oxygen, and that the derivative so formed is hydrolysed, forming diketopimelic acid, hydrochloric acid, and mercuric oxychloride, the two latter then regenerating mercuric chloride.

Pyran-2 : 6-dicarboxylic acid suspended in carbon disulphide or acetic acid, absorbs bromine, forming a *dibromide* which separates from ethyl acetate in colourless crystals containing 1 mol. of the ester. From the latter, the dibromide may be obtained as a colourless, crystalline powder, m. p. 205° (decomp.), by heating at 100°. It is readily soluble in water, which hydrolyses it, even in the cold, probably with the fission of the pyran ring. It displaces iodine from iodides in presence of alcohol or water, and in the former case regenerates the acid, which is also formed in presence of water under certain conditions. The reaction in alcohol may be employed as an iodometric method of estimating the dibromide. Attempts were made to form the corresponding pyryl salt by elimination of a mol. of hydrogen bromide, but these were unsuccessful, the elimination of the hydrogen bromide leading to complete decomposition. These results when compared with those of Fosse (*loc. cit.*), Bülow and Wagner (Abstr., 1901, i, 400), indicate that when the pyran nucleus is associated with the naphthalene nucleus the atoms of hydrogen in the 4-position with respect to the cyclic oxygen are more mobile than they are in simple pyran derivatives such as those now studied.

4-*Methylpyran*-2 : 6-*dicarboxylic acid*, m. p. about 260° (decomp.), obtained from β-methyl-$\alpha\epsilon$-diketopimelic acid, separates from warm water in small, colourless crystals. The *methyl* ester, m. p. 79—80°, crystallises from dilute alcohol; the *dibromide*, obtained by the addition of bromine to the acid suspended in acetic acid, decomposes about 190°, and separates from a mixture of ethyl acetate and light petroleum as a colourless powder. Its properties are similar to those of the dibromide of the lower homologue.

4-*Ethylpyran*-2 : 6-*dicarboxylic acid*, m. p. about 225° (decomp.), crystallises from warm acetic acid; the *methyl* ester, m. p. 64°, forms faintly yellow, long needles from dilute alcohol. 4-n-*Hexylpyran-2 : 6-dicarboxylic acid*, m. p. 220° (decomp.), crystallises from dilute alcohol in long needles containing $1H_2O$. The *methyl* ester, m. p. 72°, crystallises from dilute alcohol in long, slender needles.

T. A. H.

Rupture of the Furan Ring in Catechin.

Stanislaus von Kostanecki and Victor Lampe (*Ber.*, 1907, **40**, 720—722. Compare this vol., i, 73).—Catechin tetramethyl ether is reduced by sodium and alcohol to an oil which by treatment with methyl sulphate yields *deoxyhydrocatechin pentamethyl ether* (2 : 4 : 6 : 3′ : 4′*-pentamethoxy-3-ethyldiphenylmethane*), $C_6H_3(OMe)_2\cdot CH_2\cdot C_6H(OMe)_3Et$, m. p. 83—84°, which crystallises in colourless, prismatic needles. The same reducing agent converts benzhydrol into diphenylmethane; leucobenzophloroglucinol trimethyl ether into 2 : 4 : 6*-trimethoxydiphenylmethane*, m. p. 91—93°, and leucomaclurin pentamethyl ether into 2 : 4 : 6 : 3′ : 4′*-pentamethoxydiphenylmethane*, m. p. 107—108°.

For a similar rupture of the coumaran ring, compare Alexander, (Abstr., 1892, 1318).

C. S.

Thiophen-2-and-3-carboxylic Acids.

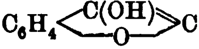
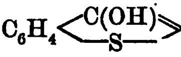
Arnold F. Holleman and Gerardus L. Voerman (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **9**, 514—524).—The authors have worked out a very satisfactory method of preparing the 2-acid. Acetothienone is first oxidised by alkaline permanganate to thienylglyoxylic acid, which is subsequently oxidised to thiophen-2-carboxylic acid by hydrogen peroxide. For the preparation of the 3-acid, 3-methylthiophen is chlorinated in the presence of phosphorus pentachloride; from the chlorinated product there is prepared an aldehyde, which is then oxidised to the thiophen-3-carboxylic acid. The yield of 3-acid obtained in this way is very poor, but is slightly better than that given by the older method, of preparation.

A study of the freezing and melting point curves for mixtures of the two acids shows that they form isomorphous mixtures, but that there is a gap in the mixture series from 25% to 61% of the 3-acid. The freezing point curve exhibits a eutectic at 42·5% of 3-acid and 111°. From the conductivity of aqueous solutions of the mixed acids, it appears unlikely that there is any condensation of the molecules of the two acids in such solutions.

The paper contains also crystallographic details of the two acids.

J. C. P.

Derivatives of Thionaphthen and Thioindigotin.

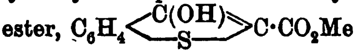
Paul Friedländer (*Annalen*, 1907, **351**, 390—420).—The resemblance of ketocoumaran,  $C_6H_4<\!\begin{matrix}C(OH)\\O\end{matrix}\!>CH$, to indoxyl, $C_6H_4<\!\begin{matrix}C(OH)\\NH\end{matrix}\!>CH$, was studied by Friedländer and Neudörfer (Abstr., 1897, i, 424; Abstr., 1899, i, 675). The author has extended the investigation to the corresponding sulphur compound,  $C_6H_4<\!\begin{matrix}C(OH)\\S\end{matrix}\!>CH$, which is found to resemble, on the one hand, indoxyl, and on the other, α-naphthol.

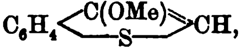
[With G. Müller.]—A detailed account of the work published previously (Abstr., 1906, i, 378). The following are new.

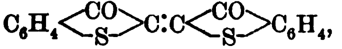
o-*Thiocyanobenzoic acid*, $CNS\cdot C_6H_4\cdot CO_2H$, formed by the action of cuprous thiocyanate on diazotised anthranilic acid, crystallises in stout, yellow needles, m. p. 154—155° (decomp.); the *methyl* ester crystallises in small, colourless needles, m. p. 76—77°, and is moderately volatile with steam. The acid is converted by evaporation with aqueous sodium sulphide into thiosalicylic acid, which with methyl sulphate and aqueous sodium hydroxide forms o-*methylthiolbenzoic acid*, $SMe\cdot C_6H_4\cdot CO_2H$; this crystallises in slender, colourless needles, m. p. 164°, and forms a *methyl* ester crystallising in colourless needles, m. p. 71°.

o-Carboxyphenylthiolacetic acid crystallises in small, white needles, m. p. 216—217° (decomp.); the *monoethyl* ester,

$$CO_2Et\cdot C_6H_4S\cdot CH_2\cdot CO_2H,$$

m. p. 137°. Whilst 2-hydroxythionaphthen-1-carboxylic acid readily decomposes, its *methyl* ester,  $C_6H_4{<}\substack{C(OH)\\S}{>}C\cdot CO_2Me$, formed by the action of sodium ethoxide on methyl *o*-carbmethoxyphenylthiolacetate, is stable; it crystallises in leaflets, m. p. 104°.

2-*Methoxythionaphthen*,  $C_6H_4{<}\substack{C(OMe)\\S}{>}CH$, prepared by the action of methyl sulphate on 2-hydroxythionaphthen in alkaline solution, is obtained as a volatile oil, b. p. 260—261° (almost undecomp.), and has the characteristic odour of α-methoxynaphthalene; the *picrate* forms brownish-red needles, m. p. 112°.

2-Hydroxythionaphthen resembles α-naphthol in its behaviour towards diazo-salts, the resulting azo-dyes being slightly more yellow, but differs in forming red, crystalline *condensation products* with aromatic aldehydes, ketones, and diketones at high temperatures or in presence of condensing agents in glacial acetic acid solution. Thioindigotin,  $C_6H_4{<}\substack{CO\\S}{>}C{:}C{<}\substack{CO\\S}{>}C_6H_4$, prepared by oxidation of 2-hydroxythionaphthen by means of potassium ferricyanide, ferric chloride, chromates, or organic nitro-compounds, melts above 280°, and on reduction yields a yellow *leuco*-compound which is soluble in aqueous alkalis, forming a solution which dyes textile fibres a fast red. On oxidation, 2-hydroxythionaphthen-1-carboxylic acid yields a bluish-violet dye, which can be converted into thioindigotin.

Derivatives of Aminothionaphthens.—[With A. Laske.]—The constitution of 2-keto-3 : 4-dihydro-1 : 4-benzothiazine (Unger and Graff, Abstr., 1898, i, 96) is confirmed by formation of the substance on reduction of *o*-nitrophenylthiolacetic acid. The ketodihydrobenzothiazine is prepared best by reduction of *o*-aniline disulphide with zinc dust and acid, and treatment of the filtered product with chloroacetic acid; when boiled with aqueous sodium hydroxides and neutralised with ice and hydrochloric acid, it yields o-*aminophenylthiolacetic acid*, which separates in colourless needles, but redissolves, forming the *hydrochloride*, $CO_2H\cdot CH_2\cdot S\cdot C_6H_4\cdot NH_2,HCl$, and gradually loses water being converted into the benzothiazine.

o-*Cyanophenylthiolacetic acid*, $CN\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$, prepared by the action of copper sulphate and potassium cyanide on diazotised *o*-aminophenylthiolacetic acid, crystallises from water in yellow needles, m. p. 140°, and forms easily soluble *alkali* salts; the *methyl* ester, $CN\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2Me$, crystallises in white, glistening needles, m. p. 87—88°. When heated with 2½% aqueous alkalis, the cyano-acid is converted into 2-*aminothionaphthen*-1-*carboxylic acid*,

$$C_6H_4\left<\begin{matrix}C(NH_2)\\S\end{matrix}\right>C\cdot CO_2H,$$

which crystallises in brown needles, m. p. 140—146°, evolving carbon dioxide, and has an intense bluish-violet fluorescence in dilute solution; the *barium* salt, $(C_9H_6O_2NS)_2Ba$, crystallises in silvery leaflets. When boiled with dilute acids, the acid evolves carbon dioxide and ammonia, forming thioindoxyl, and on treatment with nitrous acids yields a *diazo*-derivative which couples with β-naphthol, forming a red *azo-dye*.

When boiled with water, made alkaline, and distilled with steam, the amino-acid yields 2-*aminothionaphthen*, $C_6H_4\left<\begin{matrix}C(NH_2)\\S\end{matrix}\right>CH$, which is obtained as a colourless oil, gradually resinifies when exposed to air, and is soluble in dilute acids; the *sulphate*, *hydrochloride*, and *platinichloride* are described. The *acetyl* derivative,

$$C_6H_4\left<\begin{matrix}C(NHAc)\\S\end{matrix}\right>CH,$$

formed from the amine or from the amino-carboxylic acid, crystallises in colourless leaflets or needles, m. p. 169°. The base resembles α-naphthylamine in giving a characteristic violet coloration with traces of nitrous acid in acetic acid solution, but differs in being readily converted by boiling water into thioindoxyl. G. Y.

Preparation of Quinine Magnesium Oxyhalides. Vereinigte Chininfabriken, Zimmer & Co. (D.R.-P. 178172).—Quinine magnesium oxyhalides are obtained on adding the alkaloid to a solution or suspension of a Grignard compound in ether, either at the ordinary or at higher temperatures. In this way the following derivatives were prepared: quinine magnesium oxychloride, $C_{20}H_{23}N_2O\cdot O\cdot MgCl$, and oxybromide. These compounds are very reactive and serve for the preparation of other quinine derivatives. G. T. M.

Preparation of Quinine Esters. Vereinigte Chininfabriken, Zimmer & Co. (D.R.-P. 178173. Compare preceding abstract).—By treating the quinine magnesium oxyhalides with acyl chlorides or acid anhydrides, the hydroxyl group of quinine becomes esterified and esters are produced.

Acetylquinine was obtained by heating these magnesium oxyhalides with acetyl chloride or acetic anhydride; quinine ethyl carbonate was prepared in a similar manner by means of ethyl chlorocarbonate, and benzoylquinine was produced from the organo-magnesium compounds and benzoyl chloride. G. T. M.

Constitution of Hordenine. Eugène Léger (*Compt. rend.*, 1907, **144**, 488—491).—The presence of the groups $OH\cdot C_6H_4-$ and

$-NMe_2$ in the formula $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NMe_2$ ascribed to hordenine has already been proved (Abstr,, 1906, i, 761; this vol., i, 151). Experimental proof is now given of the presence of the chain $\cdot CH_2\cdot CH_2\cdot$ in a para-position to the hydroxyl. When hordenine methiodide in sodium hydroxide solution is treated with methyl sulphate, methyl iodide distils, showing that the attack proceeds further than mere methylation of the phenolic hydroxyl, and in fact the product is a mixture of methyl hordenine methiodide (this vol., i, 234) and hordenine methyl sulphate. Methyl hordenine methiodide is converted by moist silver oxide into methyl hordenine methoxide, which decomposes when heated in a vacuum at 120—130°, yielding trimethylamine and *p*-vinylanisole described by Perkin (Trans., 1877, 668; 1878, 211). The formation of the latter demonstrates the presence in hordenine of the $\cdot CH_2\cdot CH_2\cdot$ group para to the hydroxyl, and leads to the supposition that the phenol obtained in the decomposition of hordenine methoxide is *p*-vinylphenol or its polymeride. A solution of the normal tartrate of hordenine is apparently not attacked by either neutral hydrogen peroxide or by the oxidising enzyme tyrosinase, but in the presence of both peroxide and enzyme, a stable, cherry-red coloration begins to appear in ten to fifteen minutes. The reaction is accelerated by addition of a few drops of 1% sodium carbonate solution. E. H.

[Carnosine and Ignotine.] FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1907, **50**, 445—448. Compare Amiradžibi and Gulewitsch, Abstr., 1900, i, 516; Gulewitsch, this vol., i, 264).—The identity of carnosine and ignotine is not regarded by the author as being established. The two appear to react differently with silver nitrate, fixed alkalis, and ammonia. J. J. S.

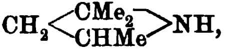
Muscle Extract. VIII. Formation of Histidine by the Decomposition of Carnosine. WLADIMIR VON GULEWITSCH (*Zeitsch. physiol. Chem.*, 1907, **50**, 535—537).—Carnosine is a histidine derivative, since when hydrolysed with barium hydroxide solution it yields this base. The other product of hydrolysis is probably alanine, and the hydrolysis may then be represented by the equation: $C_9H_{14}O_3N_4 + H_2O = C_6H_9O_2N_3 + C_3H_7O_2N$. J. J. S.

Preparation of the Alkyl Bromides of the Alkyl Ethers of Morphine. J. D. RIEDEL (D.R.-P. 175796. Compare Abstr., 1906, i, 692).—It is now found that the alkyl bromides of the alkyl ethers of morphine can be obtained by adding a metallic bromide to the aqueous solution of the dialkyl sulphate of the morphine ether, concentrating or evaporating to dryness and extracting the residue with acetone, or methyl or ethyl alcohol.

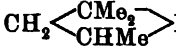
Codeine dissolved in chloroform was treated with ethyl sulphate, the solution evaporated, the residue treated with ether, and the resulting oil dissolved in water containing potassium bromide; the aqueous solution was then evaporated to dryness and the final residue extracted with methyl or ethyl alcohol. The codeine ethobromide was isolated by concentrating the alcoholic solution. Ethylmorphine, ethobromide, and codeine methobromide were prepared similarly.

G. T. M.

Derivatives of Diacetonalkamines. V. Moritz Kohn *Annalen*, 1907, 351, 134—150. Compare Abstr., 1904, i, 378, 932, 933; 1905, i, 928).—Kahan (Abstr., 1897, i, 494) having shown that diacetonalkamine combines with hydrogen bromide forming δ-bromo-β-amino-β-methylpentane hydrobromide, it was to be expected that methyldiacetonalkamine, $OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NHMe$, would be converted similarly into *δ-bromo-β-methylamino-β-methylpentane hydrobromide*, $CHMeBr\cdot CH_2\cdot CMe_2\cdot NHMe,HBr$. That this substance is contained in the resinous product of the reaction is shown by its conversion on treatment with concentrated aqueous potassium hydroxide into a volatile mono-acid *base*, $C_7H_{15}N$, the analogue of which, $C_6H_{13}N$, is formed by the action of cooled 33% potassium hydroxide on δ-bromo-β-amino-β-methylpentane hydrobromide. This *base* is 2 : 4 : 4-*trimethyltrimethylenimine*,

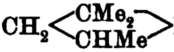


$$CH_2\left<\begin{matrix}CMe_2\\CHMe\end{matrix}\right>NH,$$

as it forms a *nitroso*-derivative, a *dithiocarbamate*, and a quaternary *iodide*, which is identical with the *additive* compound of methyl iodide and the base, $C_7H_{15}N$; this must be 1 : 2 : 4 : 4-*tetramethyltrimethylenimine*,  $CH_2\left<\begin{matrix}CMe_2\\CHMe\end{matrix}\right>NMe$. These bases are the first known alkyl derivatives of trimethylenimine (Howard and Marckwald, Abstr., 1899, i, 749). They differ from ethylenimine (Gabriel and Stelzner, Abstr., 1896, i, 121) and *N*-methylethylenimine (Marckwald and Frobenius, Abstr., 1902, i, 22) in that the ring remains intact on alkylation.

2 : 4 : 4-*Trimethyltrimethylenimine* forms a colourless oil, b. p. 86—88°, which is miscible with water, developing heat, and has an intense amine-like odour; the *aurichloride*, $C_6H_{13}N,HAuCl_4$, forms glistening needles, m. p. 124—126°; the *picrate*, $C_{12}H_{16}O_7N_4$, forms needles and plates, m. p. 140—143°. The *nitroso*-derivative, $C_6H_{12}ON_2$, is obtained as an aromatic, yellow oil, b. p. 94—95°/20—21 mm. or 198—201°/751 mm. 2 : 4 : 4-*Trimethyltrimethylenimine*, 2 : 4 : 4-*trimethyltrimethyleniminedithiocarbamate*, $C_{13}H_{26}N_2S_2$, prepared by the action of carbon disulphide on the base in cooled ethereal solution, forms white crystals, m. p. 130—133°.

1 : 2 : 4 : 4-*Tetramethyltrimethylenimine*, b. p. 93—97°, closely resembles the 2 : 4 : 4-trimethyl base; the *aurichloride*, $C_7H_{15}N,HAuCl_4$, m. p. 148—152°; the *picrate*, $C_{18}H_{18}O_7N_4$, crystallises in slender needles, m. p. 196° (decomp.); the *platinichloride*, $(C_{17}H_{15}N)_2,H_2PtCl_6$, was analysed.

The *methiodide*,  $CH_2\left<\begin{matrix}CMe_2\\CHMe\end{matrix}\right>NMe_2I$, formed by the action of methyl iodide on the 2 : 4 : 4-trimethyl- or 1 : 2 : 4 : 4-tetramethyl-base in ethereal solution, on successive treatment with silver chloride and auric chloride forms the *aurichloride*, $C_8H_{17}N,HAuCl_4$, which is obtained as a yellow, crystalline powder, m. p. 176° (decomp.);

the *platinichloride*, $(C_8H_{17}N)_2,H_2PtCl_6$, forms a yellowish-red precipitate.

On successive treatment with ethyl iodide and silver and auric chlorides, the 1 : 2 : 4 : 4-tetramethyl-base forms the *aurichloride*,

$$C_9H_{19}N,HAuCl_4,$$

m. p. 161—163° (decomp.); the *platinichloride*, $(C_9H_{19}N)_2,H_2PtCl_6$, forms glistening, granular crystals.

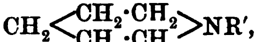
The *ammonium base*, formed by the action of moist silver oxide on the methiodide, loses H_2O when distilled, yielding an unsaturated *base*, $C_8H_{17}N$, which is obtained as a colourless, mobile liquid, b. p. 136—139°/750 mm.; the *aurichloride*, $C_8H_{17}N,HAuCl_4$, is decomposed by hot water; the *platinichloride*, $(C_8H_{17}N)_2,H_2PtCl_6$, light yellow crystals, intumescing when heated; the *picrate*, $C_{14}H_{20}O_7N_4$, thin needles, m. p. 121—124°. With methyl iodide the unsaturated base forms an *additive* compound, from with are obtained an *aurichloride*, $C_9H_{19}N,HAuCl_4$, as a yellow precipitate, and a *platinichloride*,

$$(C_9H_{19}N)_2,H_2PtCl_6,$$

crystallising in prisms or needles. In the same manner, by way of the *additive* compound of ethyl iodide and the unsaturated base, are formed the *aurichloride*, $C_{10}H_{21}N,HAuCl_4$, obtained as a yellow precipitate, and the *platinichloride*, $(C_{10}H_{21}N)_2,H_2PtCl_6$, crystallising in needles.

When treated with silver oxide and water, the methyl iodide *additive* product of the unsaturated base yields an *ammonium base*, $C_6H_{11}NMe_3{\cdot}OH$, which on distillation with water decomposes, forming trimethylamine, water, and a *hydrocarbon*, C_6H_{10}; this is a colourless, mobile liquid, b. p. 74—75°. G. Y.

Formation of 1-Phenyl-5-Methylpyrrolidone by the Simultaneous Electrolytic Reduction of Lævulic Acid and Nitrobenzene. Bruno Emmert (*Ber.*, 1907, 40, 912—916).—The author expected that γ-anilinovaleric acid would be one of the products obtained on reducing nitrobenzene and lævulic acid in an electrolytic cell using a mercury cathode. This is not formed, but a 40% yield of 1-*phenyl-5-methylpyrrolidone*, C_4NH_5MePhO, its internal anhydride is obtained as a colourless oil, b. p. 320·5° (corr.)/752 mm., 178·5°/15 mm. By cooling with solid carbon dioxide, it solidifies, m. p. 52—54°, but the liquid exhibits the phenomena of supercooling to a marked extent. It behaves like pyrrolidone (compare Tafel, Abstr., 1900, i, 557), and its constitution was established by preparing it from γ-bromovaleric acid and aniline. W. R.

Steric Hindrance of Ring-formation by *o*-Substituting Groups. Max Scholtz and E. Wassermann (*Ber.*, 1907, 40, 852—858. Compare Abstr., 1898, i, 305, 383, 471, 565; 1899, i, 881; Scholtz and Friemehlt, Abstr., 1899, i, 541; v. Braun, Abstr., 1904, i, 841).—It has been shown previously that *o*-xylylene dibromide and trimethylene dibromide react with *o*-substituted primary aromatic amines, forming substituted diamines, but with other primary aromatic amines forming cylic compounds. It is now found that αε-dibromopentane behaves towards primary aromatic amines in the same manner; the products formed with *m*- and *p*-substituted amines being derivatives of piperidine,  $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NR'$, whilst those with *o*-substituted amines are pentamethylenediamines, $NHR\cdot[CH_2]_5\cdot NHR$. *o*-Naphthylamine behaves as an *o*-, *β*-naphthylamine as a *m*- or *p*-substituted amine. The reaction takes place, but only slowly, with *oo*-disubstituted amines such as *o*-amino-*m*-xylidine. The following new substances have been prepared.

Pentamethylenedi-o-*toluidine*, $R = C_7H_7(o)$, colourless prisms, m. p. 76—77°, b. p. 290—291°/20 mm., forms a sparingly soluble *sulphate*; 1-m-*tolylpiperidine*, $R' = C_7H_7(m)$, colourless prisms, m. p. 126°; 1-p-*tolylpiperidine*, needles, m. p. 122°; *pentamethylenedi*-o-*nitroaniline*, $R = NO_2\cdot C_6H_4(o)$, red needles, m. p. 55—57°; 1-p-*nitrophenylpiperidine*, $R' = NO_2\cdot C_6H_4(o)$, yellow needles, m. p. 114°; *pentamethylenedicumidine*, $R = C_6H_2Me_3[Me_3 = 2:4:5]$, colourless leaflets, m. p. 115—116°; *pentamethylenedi-a-naphthylamine*, $R = C_{10}H_7$, yellow needles, m. p. 61°; 1-*β-naphthylpiperidine*, $R' = C_{10}H_7$, leaflets, m. p. 54°; *pentamethylenedi*-o-*chloroaniline*, $R = C_6H_4Cl(o)$, colourless crystals, m. p. above 300°; 1-p-*chlorophenylpiperidine*, $R' = C_6H_4Cl(p)$, scales, m. p. 208°; *pentamethylenedi*-o-*methoxyaniline*,

$$R = C_6H_4\cdot OMe(o),$$

colourless prisms, m. p. 131°; 1-p-*methoxyphenylpiperidine*,

$$R' = C_6H_4\cdot OMe(p),$$

glistening crystals, m. p. 37°; *pentamethylenedi*-o-*carboxyaniline*,

$$R = \cdot C_6H_4\cdot CO_2H(o),$$

slender needles, m. p. 171°; m-*piperidylbenzoic acid*,

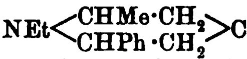
$$R' = \cdot C_6H_4\cdot CO_2H(m),$$

colourless needles, m. p. 227°, forms yellow solutions in aqueous alkalis; the *barium* and *lead* salts are yellow and dissolve to a colourless solution in acetic acid; p-*piperidylbenzoic acid*, colourless needles, m. p. 188°; *pentamethylenedi*-2 m-*xylidine*, $R = C_6H_3Me_2[Me_2 = 2:6]$, colourless leaflets, m. p. 228°. G. Y.

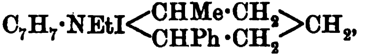
Stereoisomerism of Compounds containing a Quinquevalent Asymmetric Nitrogen Atom and an Asymmetric Carbon Atom. MAX SCHOLTZ and E. WASSERMANN (*Ber.*, 1907, **40**, 685—690).—It had been shown previously (Abstr., 1904, i, 1044; 1905, i, 296, 473) that, when an asymmetric nitrogen atom is generated in an optically active compound which owes its optical activity to the presence of an asymmetric carbon atom, the case is exactly the same as when an additional asymmetric carbon atom is generated in a compound, already optically active in virtue of asymmetric carbon; two compounds are formed, differing from one another in solubility, melting point, and specific rotation.

2-Phenyl-6-methyl-1-ethylpiperidine has two asymmetric carbon atoms. The addition of benzyl iodide to the active forms of this compound has been studied—a change in which the nitrogen atom becomes asymmetric.

Since there are two asymmetric carbon atoms in *dl*-2-phenyl-6-methylpiperidine, two *dl*-compounds are known. The one, which forms the more sparingly soluble hydrochloride (m. p. 215—216°), was resolved into its optically active components as described previously (Abstr., 1901, i, 4[illegible]1).

l-2-*Phenyl*-6-*methyl*-1-*ethylpiperidine*,  $\mathrm{NEt}<\substack{\mathrm{CHMe\cdot CH_2}\\ \mathrm{CHPh\cdot CH_2}}>\mathrm{CH_2}$, obtained by the ethylation of the *sec.*-*l*-base in question with ethyl iodide and potassium hydroxide, has b. p. 258°/760 mm. and 131°/12 mm. It has D_4^{20} 0·9519 and $[\alpha]_D$ − 64·5°. When the mixture with benzoyl iodide remains at the ordinary temperature for two days, a mixture of two compounds is formed, which may be separated by treatment with a mixture of chloroform and ether.

α-*l*-2-*Phenyl*-1-*benzyl*-6-*methyl*-1-*ethylpiperidinium iodide*,



$$\mathrm{C_7H_7\cdot NEtI}<\substack{\mathrm{CHMe\cdot CH_2}\\ \mathrm{CHPh\cdot CH_2}}>\mathrm{CH_2},$$

has m. p. 184°, and in methyl-alcoholic solution has $[\alpha]_D^{16}$ − 7·35° ($c = 6·8$).

β-*l*-2-*Phenyl*-1-*benzyl*-6-*methyl*-1-*ethylpiperidinium iodide* has m. p. 205°, and is formed in larger amount than the α-compound; in methyl alcoholic solution has $[\alpha]_D^{15}$ − 11·03° ($c = 6·8$).

d-2-*Phenyl*-6-*methyl*-1-*ethylpiperidine* has b. p. 257°, D^{20} 0·9517, $[\alpha]_D^{15}$ + 64·1°. The mixture of piperidinium iodides obtained from it by the action of benzyl iodide was separated by means of chloroform, the more sparingly soluble of the two being α-d-2-*phenyl*-1-*benzyl*-6-*methyl*-1-*ethylpiperidinium iodide*, m. p. 184°. In methyl-alcoholic solution it has $[\alpha]_D^{15}$ + 7·35° ($c = 6·8$).

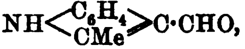
β-d-2-*Phenyl*-1-*benzyl*-6-*methyl*-1-*ethylpiperidinium iodide* has m. p. 205° and $[\alpha]_D^{15}$ + 11·03° ($c = 6·8$) in methyl-alcoholic solution.

When equal amounts of the *d*- and *l*-α-compounds are mixed in methyl-alcoholic solution and the product crystallised from water, a product with m. p. 202° was obtained. When a similar experiment was carried out with the *d*- and *l*-β-compounds, the product had the same m. p. as that of its components, namely, 205°. A. McK.

Diphenyl-4-pyridylcarbinol. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1105—1108).—*Diphenyl*-4-*pyridylcarbinol*, $\mathrm{C_5NH_4\cdot CPh_2\cdot OH}$, prepared by the action of 4-benzoylpyridine on magnesium phenyl bromide in ethereal solution, crystallises from ethyl or amyl acetate as a granular powder, m. p. 203°, and is sparingly soluble in the ordinary solvents; it acts as a base and dissolves readily in dilute mineral acids. The *platinichloride*, $\mathrm{(C_{18}H_{15}ON)_2,H_2PtCl_6}$, m. p. 188—190° (decomp.), and the *picrate*, separating from benzene with benzene of crystallisation, have been prepared.

Attempts to prepare salts of diphenyl-4-pyridylcarbinol, corresponding with the basic dyes, were unsuccessful. The carbinol dissolves, however, in concentrated sulphuric acid, giving an intense red coloration which slowly changes to a dirty brown. With a concentrated solution of zinc chloride containing hydrochloric acid, the carbinol also gives an intensely red solution, which deposits the carbinol unchanged on addition of ammonia, or becomes brown if kept.

T. H. P.

Action of Chloroform on 2-Methylindole and on Certain Pyrroles. GIUSEPPE PLANCHER and U. PONTI (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 130—135).—When 2-methylindole is acted on by sodium ethoxide and chloroform under the conditions given by Magnanini (Abstr., 1887, 1113), it yields: (1) the chloromethylquinoline, described by Magnanini (*loc. cit.*), and (2) 2-*methylindole*-3-*aldehyde* (2-*methyl*-3-*methylalindole*),  $NH{<}\genfrac{}{}{0pt}{}{C_6H_4}{CMe}{>}C\cdot CHO$, which crystallises from ethyl acetate in rosettes of slender, colourless needles, m. p. 198°. These crystals gradually change into approximately cubical crystals having the same melting point, but whether the two forms are dimorphically or tautomerically related is undecided. 2-Methylindole-3-aldehyde dissolves in water, alcohol, ether, or concentrated potassium hydroxide solution, and gives a faint red coloration with a pine splinter and hydrochloric acid, whilst when it is boiled with dilute sulphuric acid the latter first turns yellow, then red, and ultimately deposits orange-red, acicular crystals (compare Ellinger, Abstr., 1906, i, 696). The aldehyde does not reduce Fehling's solution, but gives a *semicarbazone*, $C_{11}H_{12}ON_4$, m. p. 224° (decomp.), and a p-*nitrophenylhydrazone*, m. p. 273°, or 250° if placed in a bath at that temperature; it forms a *picrate*, m. p. 181° (decomp.). Oxidation of the aldehyde with faintly alkaline permanganate solution at about 60° yields acetylanthranilic acid (*o*-acetylaminobenzoic acid), whilst in the cold, traces of 2-methylindole-3-carboxylic acid are also obtained.

The yield of 2-methylindole-3-aldehyde obtained in the above reaction may be increased by gradually adding an aqueous alcoholic solution of potassium hydroxide to a boiling solution of 2-methylindole in 95% alcohol containing excess of chloroform. T. H. P.

Steric Hindrance of Alkyl Substituted Cinchonic Acids. HANS MEYER (*Monatsh.*, 1907, **28**, 33—46. Compare Abstr., 1906, i, 107, 137, 358).—It has been shown previously that the stability of methyl esters or ethers may differ considerably from that of the corresponding ethyl compounds. It is now found that the differences in stability may outweigh the effect of steric hindrance, the hydrolysis of certain methyl esters in which steric hindrance must be assumed taking place more easily than that of analogously constituted ethyl esters not sterically hindered.

The work of Ornstein (*Diss.*, *Berlin*, 1904) and of Mulert (Abstr., 1906, i, 534) is criticised and attention drawn to the author's papers (*loc. cit.*). The action of methyl alcohol on methyl 2-chloro-3-methylcinchonate at 100° leads to the formation of the 2-hydroxy- and not of the 2-methoxy-ester. Butyrylisatin crystallises in long, yellow needles, m. p. 136°.

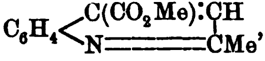
The following esters are prepared from the acids by the thionyl chloride method: *methyl 2-phenylcinchonate*, $C_9NH_5Ph\cdot CO_2Me$, forms colourless leaflets, m. p. 58°, becomes electrified when rubbed, and is converted by aqueous ammonia into the sparingly soluble *amide*, m. p. 155°; *ethyl 2-hydroxy-3-methylcinchonate*, $OH\cdot C_9NH_4Me\cdot CO_2Et$, crystallises in long needles, m. p. 167°; *ethyl* 2-*hydroxy*-3-*ethylcinchonate* crystallises in long needles, m. p. 133—134°; the *chloride* of this acid, m. p. 100°, can be recrystallised from boiling alcohol almost without change.

Hydrolysis experiments with these and similar substituted cinchonates on the water-bath gave the following results; the figures are the percentages hydrolysed by *N*-sodium carbonate and by 5% aqueous potassium hydroxide respectively: methyl cinchonate, 12, 100; methyl 3-methylcinchonate, 0, 0; methyl 2-hydroxycinchonate, 90, 100; ethyl 2-hydroxycinchonate, 60, 100; methyl 2-hydroxy-3-methylcinchonate, 45, 100; ethyl 2-hydroxy-3-methylcinchonate, 7, 100; methyl 2-hydroxy-3-ethylcinchonate, 18, 100; ethyl 2-hydroxy-3-ethylcinchonate, 0, 100.

Contrary to Fischer's rule that the presence of a group, which forms a salt with the hydrolysing agent, retards the hydrolysis (Abstr., 1899, i, 262), the hydrolysis of the cinchonates is favoured by the introduction of a hydroxyl in position 2. The influence of *o*-substitution also is noticeable; the stability of methyl 2-phenylcinchonate is remarkable in view of Findlay and Turner's observations on the acceleration of the rate of hydrolysis by the introduction of phenyl groups (Trans., 1905, 87, 747). Stress is laid on the obvious increase in the stability of the carboxyalkyl consequent on the substitution of ethyl for methyl. G. Y.

Wandering of Alkyl Groups in the Pyridine Series. Hans Meyer (*Monatsh.*, 1907, 28, 47—62. Compare Abstr., 1906, i, 604).—The 2- and 4-*O*-ethers and the 4-carboxyalkyl derivatives of pyridine and quinoline are capable of undergoing isomeric change into the corresponding *N*-alkyl compounds. In the present work the behaviour of derivatives of 2-hydroxyquinoline-3-, 2-hydroxyquinoline-4-, and 2-hydroxypyridine-5-carboxylic acids has been studied and the following general conclusions are drawn from the results.

When heated, 2-methoxy- or 2-ethoxy-3-carboxylic acids of the pyridine series lose the methyl or ethyl group and form anhydrides together with small amounts of the alkylated pyridones. 2-Alkyloxy-4-carboxylic acids of the pyridine series are converted by the action of heat into the corresponding hydroxy-esters, together with small amounts of the free acids. 2-Alkyloxypyridine-5-carboxylic acids, when heated, yield the free hydroxy-acids, together with small amounts of the alkylated pyridones. In no case does the isomeric change of the *O*- into the *N*-ether, typical of other 2-alkyloxypyridines, take place if a carbonyl or, as in methyl 2-methoxynicotinate, a carboxyalkyl group is present in the molecule. This behaviour is directly contrary to that of the ester-acids (compare Kirpal, Abstr., 1902, i, 564; 1903, i, 117, 852).

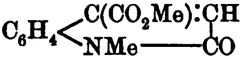
Methyl 2-*methylcinchonate*,  $C_6H_4\Big<\begin{array}{l}C(CO_2Me){:}CH\\ N{=\!=\!=\!=\!=\!=}CMe\end{array}$, m. p. 61—62°, prepared by the action of diazomethane on the acid, decomposes partially when distilled. The *amide* crystallises in colourless needles, m. p. 238°, and is converted by the action of bromine and dilute sodium hydroxide into 4-amino-2-methylquinoline.

2-Hydroxyquinoline-3-carboxylic acid is prepared best from *o*-nitrobenzylidenemalonic acid (Stuart, Trans., 1888, 53, 143), which is formed almost quantitatively by heating *o*-nitrobenzaldehyde with malonic and glacial acetic acids at 135°. The *methyl* ester,

$$OH\cdot C_9NH_5\cdot CO_2Me,$$

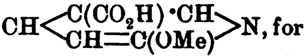
crystallises in long needles, m. p. 186°. Chlorination of the acid leads to the formation of 2-chloroquinoline-3-carboxylic acid (Friedländer and Göhring, Abstr., 1884, 1019) and a *substance* insoluble in aqueous alkalis. 2-*Methoxyquinoline*-3-*carboxylic acid*, $OMe\cdot C_9NH_5\cdot CO_2H$, formed by heating the 2-chloro-acid with sodium methoxide and methyl alcohol at 100°, crystallises in colourless needles, m. p. 182°, and when heated above its melting point yields the anhydride obtained by Friedländer and Göhring (*loc. cit.*) from 2-ethoxyquinoline-3-carboxylic acid.

It is shown that Königs and Körner's methyl derivative of hydroxycinchonic acid is methyl 2-hydroxycinchonate (Abstr., 1884, 84; Claus, Abstr., 1892, 1488; Roser, Abstr., 1893, i, 177; 1895, i, 155; Decker, Abstr., 1893, i, 365). When treated with thionyl chloride, Roser's 1-methyl-2-quinolone-4-carboxylic acid yields a crystalline *chloride* which is converted by methyl alcohol into the *methyl* ester,



$C_6H_4\left<\begin{array}{l}C(CO_2Me){:}CH\\ NMe\text{———}CO\end{array}\right.$, yellow needles, m. p. 122°.

2-*Methoxypyridine*-5-*carboxylic acid*,



$CH\left<\begin{array}{l}C(CO_2H)\cdot CH\\ CH{=}C(OMe)\end{array}\right>N$, formed by heating the 2-chloro-acid with sodium methoxide and methyl alcohol at 110°, crystallises in colourless needles, m. p. 173°, and at temperatures above 260° decomposes, forming 2-hydroxypyridine-5-carboxylic acid and traces of 2-methoxypyridine. The methyl ester, $OMe\cdot C_5NH_3\cdot CO_2Me$ (Abstr., 1906, i, 108), m. p. 42°, b. p. 256°, prepared by the action of diazomethane on the methoxy-acid, remains unchanged when heated at 330°.

G. Y.

Action of Thionyl Chloride on Quinaldinic (Quinoline-2-carboxylic) Acid.

Hans Meyer and Richard Turnau (*Monatsh.*, 1907, **28**, 153—162. Compare Meyer, Abstr., 1905, i, 155, 666; Besthorn and Ibele, Abstr., 1905, i, 612; 1906, i, 605).—Contrary to the repeated statements of Besthorn and Ibele, the action of thionyl chloride, whether freshly prepared or distilled from a previous reaction mixture, on quinoline-2-carboxylic acid leads to the formation of only one product, quinoline-2-carboxylic chloride, m. p. 175° (decomp.). The excess of thionyl chloride may be removed by treatment with formic acid with which it reacts energetically, whilst the quinoline-2-carboxylic chloride reacts with formic acid only slowly. The carboxylic chloride forms the ester in an 80%, and the amide in a 75%, yield, whereas if it were an anhydride hydrochloride as suggested by Besthorn and Ibele, it could not form more than 50% of the ester or amide.

Pyridine- and quinoline-carboxylic acids are isolated from their salts most readily by conversion into the hydrochloride or nitrate, and addition of 1 mol. of sodium hydroxide.

G. Y.

Behaviour of Arylated Naphthylamines with Formaldehyde and with Nitrous Acid.

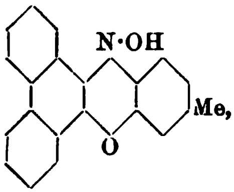
Hans T. Bucherer and Franz Seyde (*Ber.*, 1907, **40**, 859—865. Compare Abstr., 1905, i, 585).—The product, obtained by treating a hot alcoholic solution of an arylnaphthylamine with formaldehyde and a small quantity of hydrochloric acid, depends on the nature of the aryl group. If this is a para-substituted benzene nucleus, the product is a dihydronaphthacridine derivative, whereas, arylnaphthylamines containing a nucleus with a free para-position, or those of the α-series, yield dinaphthylmethane derivatives. Thus, *p*-anisyl-β-naphthylamine yields 10-*methoxy*-1 : 2-*dihydronaphthacridine*, $C_{18}H_{15}ON$, m. p. 260°, and *p*-tolyl-β-naphthylamine yields Ullmann's 10-methyl-1 : 2-dihydronaphthacridine in a pure state, m. p. 212° (compare Abstr., 1900, i, 360), which does not possess basic properties, and is oxidised readily to the corresponding acridine. On the other hand, phenyl-β-naphthylamine yields an amorphous *substance*, $C_{33}H_{26}N_2$, m. p. 80°, which has basic properties, couples with diazo salts, and appears to be diphenyldiaminodinaphthylmethane. *p*-Tolyl-α-naphthylamine yields a *substance*, $C_{35}H_{30}N_2$, of a similar character to the preceding dinaphthylmethane derivative.

By the action of nitrous acid on a hot alcoholic solution of *p*-tolyl-β-naphthylamine, a *substance*, $C_{17}H_{13}N$, m. p. 223—224°, is obtained, which separates from benzene in red needles, forms a white, crystalline *hydrochloride*, and an *acetyl* derivative, m. p. 231—232°; the examination of the substance is in progress. C. S.

The Oxime of 1-Methylcinchotoxine and its Transformation by the Beckmann Reaction. WILHELM KOENIGS (*Ber.*, 1907, 40, 648—652)—[with KARL BERNHART and JOSEF IBELE.]—Rabe's formula for cinchotoxine, $C_9NH_6\cdot CO\cdot CH_2\cdot CH_2\cdot C_7H_{12}N$ (this vol., i, 78; compare also Abstr., 1905, i, 811), where C_9NH_6 is the quinoline and $C_7H_{12}N$ the 3-vinylpiperidine nucleus, differs from Koenigs, in that it has the carbonyl adjacent to the quinoline group, whereas the author supposed it to be between the two methylene groups. In order to decide this, the *oxime* of 1-methylcinchotoxine, m. p. 70—110°, was prepared, and on hydrolysing the product from the Beckmann change a 6% yield of cinchoninic acid and a 43% yield of 4-aminoquinoline (Hoogewerff and van Dorp, Abstr., 1892, i, 725) was obtained which supports Rabe's formula for cinchotoxine. W. R.

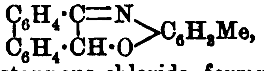
Azoxonium Compounds. IV. Phenanthraquinone Azoxine Derivatives. FRIEDRICH KEHRMANN and ABERT WINKELMANN (*Ber.*, 1907, 40, 613—623. Compare Abstr., 1901, i, 484, 1905, i, 930, 949).—This is a continuation of the inquiry into the action of aminophenols on phenanthraquinone including the aminocresols and nitro-*o*-aminophenols; all show similar changes, the colourless ψ-bases giving rise to intensely coloured azoxonium salts and yellow ψ-salts.

Phenanthraquinone and *o*-amino-*m*-cresol in boiling benzene condense to form the *ψ-base*, crystallising in white needles decomposing at 200° without melting. When this is dissolved in a mixture of 2 parts alcohol and 1 part benzene and the bulk of the benzene removed by boiling, almost colourless aggregates of needles, m. p. 95°, separate. Sulphuric acid dissolves the compound with a blue coloration, the solution on carefully adding



ice deposits yellow crystals; these give the ψ-base on further washing with water. The yellow sulphate could not be analysed, but the corresponding *yellow nitrate* was. The unstable *azoxonium nitrate* is almost black.

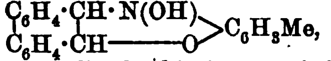
ψ-3-Methylphenanthraphenazoxine



$$\begin{matrix} C_6H_4\cdot C{=}N \\ | \quad\ | \\ C_6H_4\cdot CH\cdot O \end{matrix}\!\!>C_6H_3Me,$$

obtained by the reduction of the ψ-base with stannous chloride, forms greenish-yellow needles, m. p. 163—164°.

Hydroxydihydro-3-methylphenanthraphenazoxine,

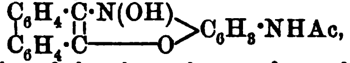


$$\begin{matrix} C_6H_4\cdot CH\cdot N(OH) \\ | \quad\ | \\ C_6H_4\cdot CH\text{———}O \end{matrix}\!\!>C_6H_3Me,$$

is formed when the ψ-base dissolved in benzene is heated with phenylhydrazine. It is oxidised at 100°, losing two hydrogen atoms, and is a white, glistening, felt-like substance.

The *ψ-base* from *o*-amino-*p*-cresol, $C_{21}H_{15}O_2N$, forms white leaflets, m. p. 195° (decomp.). *ψ-2-Methylphenanthraphenazoxine*, $C_{21}H_{15}ON$, forms greenish-yellow needles, and gives a green fluorescence in alcoholic solution.

The *ψ-base* derived from 5-nitro-3-amino-*p*-cresol, $C_{21}H_{14}O_4N_2$, forms slender, greenish-grey needles, m. p. 202—204° (decomp.). The *ψ-base* from 4-nitro-2-aminophenol, $C_{20}H_{12}O_4N_2$, white needles, m. p. 224—225°, gives a *dihydro*-derivative, $C_{20}H_{14}O_4N_2$, which forms orange needles. The *acetylamino*-derivative,

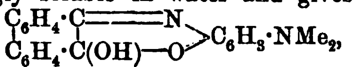


$$\begin{matrix} C_6H_4\cdot C\cdot N(OH) \\ | \quad\ \| \\ C_6H_4\cdot C\text{———}O \end{matrix}\!\!>C_6H_3\cdot NHAc,$$

obtained by reduction of the nitro-ψ-base and acetylation, is a yellowish-white powder, m. p. 220° (decomp.).

The ψ-base from 3-nitro-2-aminophenol, $C_{20}H_{12}O_4N_2$, m. p. 220° (decomp.), gives the corresponding *azoxine*, which forms bluish-violet needles from pyridine, and decomposes at 220° without melting.

3-Aminophenanthraphenazoxonium chloride is dark violet, and in aqueous solution is partially hydrolysed. An aqueous solution colours ether yellow when shaken with it. This is due to a yellow *ψ-base* which is obtained as a brownish-yellow mass on decomposing the chloride with sodium acetate and a few drops of sodium hydroxide. 3-*Dimethylaminophenanthraphenazoxonium* salts were obtained from Frie's zinc chloride double salt (D.R.-P. 130743). The *nitrate* is sparingly soluble in water and gives on long keeping the yellow *ψ-base*,



$$\begin{matrix} C_6H_4\cdot C\text{=====}N \\ | \quad\ | \\ C_6H_4\cdot C(OH)\text{—}O \end{matrix}\!\!>C_6H_3\cdot NMe_2,$$

purified in the same way as the parent substance, it forms lemon-yellow crystals, m. p. 180° (decomp.).

W. R.

Preparation of *NN'*-Dialkylmethylenediaryldiamines and Homologues. EMIL FRÖHLICH (*Ber.*, 1907, **40**, 762—765).—The author describes the preparation of a homologous series of asymmetrical diammonium bases, the first member being *methylenedi-methylaniline*, $CH_2(NMePh)_2$, obtained from methylaniline and formaldehyde as a yellow, viscid oil, b. p. 227°/33 mm.

Methylenedi-ethylaniline, $CH_2(NEtPh)_2$, obtained from ethylaniline and formaldehyde, separates from light petroleum in prisms, m. p. 76—77°.

Ethylenedi-methylaniline, $C_2H_4(NMePh)_2$, obtained from methylaniline and ethylene dibromide, is first obtained as a yellow, viscid oil, b. p. 245°/45 mm., which soon solidifies and may be crystallised from light petroleum as prisms, m. p. 47—48°. Its *picrate* has m. p. 180° (decomp.).

Ethylenedi-ethylaniline, $C_2H_4(NEtPh)_2$, obtained from ethylaniline and ethylene dibromide, has b. p. 245°/45 mm., and separates from light petroleum in prism, m. p. 75°. Its *picrate* has m. p. 189—190° (decomp.).

Trimethylenedi-methylaniline, $CH_2(CH_2{\cdot}NMePh)_2$, obtained from methylaniline and trimethylene bromide, has b. p. 270—272°/70 mm., and separates from light petroleum in prisms, m. p. 46—47°. Its *picrate* has m. p. 183—184° (decomp.).

Trimethylenedi-ethylaniline, $CH_2(CH_2{\cdot}NEtPh)_2$, obtained from ethylaniline and trimethylene bromide, is a yellow, viscid oil, b. p. 245—247°/30 mm. Its *picrate* has m. p. 177° (decomp.).

A. McK.

Preparation of 4′-Nitroso-4-acetylaminodiphenylamine and its *o*-Sulphonic Acid. LEOPOLD CASSELLA & Co. (D.R.-P. 176046).

—*4′-Nitroso-4-acetylaminodiphenylamine*, $NO{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NHAc$, prepared by adding concentrated aqueous sodium nitrite to an alcoholic hydrochloric acid solution of 4-acetylaminodiphenylamine is precipitated with brine as a brown deposit soluble in alkalis and reprecipitated by acids, and dissolving in alcohol to a reddish-brown solution. *4′-Nitroso-4-acetylaminodiphenylamine-2-sulphonic acid* is produced similarly, and consists of a brown, crystalline powder which dissolves only sparingly in water and dilute acids, but is somewhat soluble in alcohol. Its alkali salts are readily soluble and separate from their concentrated solutions in brown crystals. These nitroso-compounds are of great technical importance in the production of safranines.

G. T. M.

Action of Mono- and Di-chloroacetic Acids on Primary Hydrazines. Hindrance of Chemical Reactions. MAX BUSCH and EDUARD MEUSSDÖRFFER (*J. pr. Chem.*, 1907, [ii], 75, 121—141. Compare Abstr., 1904, i, 97; Fries, Abstr., 1906, i, 644).

—The action of chloroacetic acid on arylhydrazines, under the conditions which with phenylhydrazine lead to the formation of *as*-phenylhydrazinoacetic acid, was investigated with the object of determining if the product is always an *as*-hydrazinoacetic acid, $NH_2{\cdot}NR{\cdot}CH_2{\cdot}CO_2H$. It has been found that *o*-tolyl-, *o*-anisyl-, *o*-chlorophenyl-, and *a*-naphthylhydrazines, which might have been expected to yield *s*-hydrazinoacetic acids, $NHR{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, do not react with chloroacetic acid. This failure of the reaction might be ascribed to steric hindrance, but it is found further that β-naphthylhydrazine does not enter into the reaction, whilst 4-*m*-xylylhydrazine, despite the presence of an *o*-methyl, yields a mixture of the two isomeric xylylhydrazinoacetic acids.

All *o*- and *p*-substituted phenylhydrazines which have been studied react with dichloroacetic acid, forming hydrazones of glyoxylic acid, $NHR\cdot N\colon CH\cdot CO_2H$; the rate of this reaction is retarded and the yields diminished by the presence of an *o*-bromine, still more by that of an *o*-iodine, atom. The influence of an *o*-substituting group may extend apparently even to the β-nitrogen atom; the formation of arylazoformaldoximes, $NR\colon N\cdot CH\colon N\cdot OH$, by the action of nitrous acid on arylhydrazones of glyoxylic acid (Busch and Wolbring, Abstr., 1905, i, 493) takes place equally well with *o*- and *p*-chlorophenyl-, or with *o*-anisyl- and *p*-nitrophenyl-hydrazones of glyoxylic acid, but fails with the *o*-bromo-, *o*-iodo-, and *o*-nitro-phenylhydrazones. This could be explained by assuming the reaction to take place in two stages, the intermediate product being the nitroso-derivative,

$$NO\cdot NR\cdot N\colon CH\cdot CO_2H,$$

the formation of which would be sterically hindered by the presence of *o*-groups. The difference in the behaviour of the *o*-chloro-, and the *o*-bromo-, and *o*-iodo-compounds must be the result of the differences in the atomic volumes.

Whilst in the presence of potassium carbonate, chloroacetic acid and phenylhydrazine yield only the *as*-hydrazino-acid, in presence of an alkali hydroxide the acid acts in the same manner as the ester, a mixture of the *s*- and *as*-hydrazinoacetic acids being formed.

In one experiment with *o*-tolylhydrazine, a very small amount of a *tolylhydrazinoacetic acid*, $C_9H_{12}O_2N_2$, forming yellowish-white crystals, m. p. 140° (decomp.), was obtained. *o*-Tolylhydrazine does not react, or reacts to only a small extent with ethyl chloroacetate.

s-4-m-*Xylylhydrazinoacetic acid* crystallises from dilute alcohol in glistening leaflets, m. p. 162—163°. The as-*isomeride* crystallises in glistening leaflets, m. p. 178°, evolves nitrogen with Fehling's solution, and forms a m-*nitrobenzylidene* derivative, crystallising in yellow needles, m. p. 151°.

as-p-*Tolylhydrazinoacetic acid* crystallises in white needles, m. p. 158°. The *benzylidene* derivative crystallises in yellow needles, m. p. 166°; the *m*-nitrobenzylidene derivative, yellow needles, m. p. 191°. The *ethyl* ester crystallises from ether in slender, white needles, m. p. 123—125°, and forms a m-*nitrobenzylidene* derivative, yellow needles, m. p. 123—124°.

as-m-*Tolylhydrazinoacetic acid* crystallises in white leaflets, m. p. 160° (decomp.); the m-*nitrobenzylidene* derivative crystallises from alcohol in yellow prisms, m. p. 189° (decomp.); the benzylidene derivative forms greenish-yellow needles, m. p. 158° (decomp.).

as-p-*Anisylhydrazinoacetic acid* crystallises in white leaflets, m. p. 137° (decomp.), evolves nitrogen with Fehling's solution, and forms a m-*nitrobenzylidene* derivative, crystallising in yellow needles, m. p. 159°.

as-p-*Bromophenylhydrazinoacetic acid* crystallises in white needles,

m. p. 138° (decomp.); the m-*nitrobenzylidene* derivative forms yellow needles, m. p. 189° (decomp.).

The action of 2 mols. of *p*-bromophenylhydrazine on 1 mol. of potassium chloroacetate leads to the formation of a mixture of the two hydrazinoacetic acids. s-p-*Bromohydrazinoacetic acid*, m. p. 150°, is insoluble in aqueous oxalic acid, and reduces Fehling's solution without evolution of nitrogen.

Glyoxylic acid-o-*anisylhydrazone* crystallises in yellow, microscopic plates, m. p. about 115°, decomposing at a slightly higher temperature. *o*-Anisylazoformaldoxime, m. p. 153—154° (decomp.).

o-*Chlorophenyl*-m-*nitrobenzylidenehydrazine* forms yellow needles, m. p. 150°. *Glyoxylic acid*-o-*chlorophenylhydrazone* crystallises in lemon-yellow needles, m. p. 145° (decomp.).

Glyoxylic acid-p-*chlorophenylhydrazone* forms flat spears, m. p. 142° (decomp.).

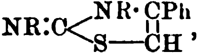
o-*Bromophenylhydrazine*, prepared from *o*-bromoaniline, is obtained as a viscid oil solidifying to white needles, m. p. 48°. Glyoxylic acid-*o*-bromophenylhydrazone is formed in two stereoisomeric modifications of which the one, m. p. 160°, is identical with Busch and Wolbring's product from diazo-*o*-bromophenyl acetate (*loc. cit.*); the second *stereoisomeride*, which is soluble in benzene, crystallises in orange-yellow needles, m. p. 154°. Both modifications yield at most only traces of the corresponding azoformaldoxime.

o-*Iodophenyl*-m-*nitrobenzylidenehydrazine* crystallises in yellow needles, m. p. 170°.

p-*Nitrophenylazoformaldoxime*, formed from the *p*-nitrophenylhydrazone of ammonium glyoxylate (Busch and Wolbring, *loc. cit.*), crystallises from a mixture of ether and light petroleum in red needles, m. p. 118° (decomp.). G. Y.

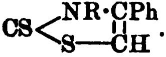
Action of Bromoacetophenone on Thiocarbamides. REINHOLD VON WALTHER (*J. pr. Chem.*, 1907, [ii], 75, 187—199. Compare Traumann, Abstr., 1889, 414).—It is considered that in the formation of iminothiazolines, the first stage of the reaction consists of the addition of the α-halogenoketone to the sulphur atom of the thiocarbamide, the loss of the hydrogen haloid forming the second stage.

[With H. GREIFENHAGEN.]—The action of bromoacetophenone on *s*-diarylthiocarbamides in alcoholic solution on the water-bath leads to the formation of 2-arylimino-4-phenyl-3-aryl-2 : 3-thiazolines,



$$\mathrm{NR{:}C}\begin{array}{l}\diagup\mathrm{NR\cdot CPh}\\ \diagdown\mathrm{S{-}{-}CH}\end{array},$$

which are strong, monoacid bases, are stable towards hydrochloric acid, and, when heated with carbon disulphide in a sealed tube at 200°, yield the corresponding feebly basic 2-thio-4-phenyl-3 aryl-2 : 3-thiazolines,



$$\mathrm{CS}\begin{array}{l}\diagup\mathrm{NR\cdot CPh}\\ \diagdown\mathrm{S{-}{-}CH}\end{array}.$$

The following iminothiazolines have been prepared; the temperatures are melting points.

From *s*-diphenylthiocarbamide, R = Ph: long, white needles; the *hydrobromide*, $C_{21}H_{16}N_2S,HBr$, prisms, 276°; the *platinichloride*, $(C_{21}H_{16}N_2S)_2,H_2PtCl_6$, a brown, crystalline precipitate; the picrate, $C_{21}H_{16}N_2S,C_6H_3O_7N_3$, orange-yellow prisms, 173°. From *s*-di-*p*-tolylthiocarbamide,

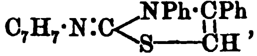
$$R = C_7H_7(p):$$

long, white needles, 188°; the *hydrochloride*, prisms, 235°; the *hydrobromide* remains unchanged at 242°; the *platinichloride*, a brown, crystalline precipitate. From *s*-di-*o*-tolylthiocarbamide, $R = C_6H_4Me(o)$: colourless leaflets, 120°; the *platinichloride* and the *picrate*, 208°, were analysed. From *s*-di-*m*-tolylthiocarbamide, $R = C_6H_4Me(m)$: slender needles, 103°; the *platinichloride* was analysed.

The following thiothiazolines are described; the temperatures are melting points.

$R = Ph$: white needles, 148°; $R = C_6H_4Me(p)$: white needles, 146°; $R = C_6H_4Me(o)$: silvery leaflets, 146°; $R = C_6H_4Me(m)$: white needles, 195°.

Of the isomeric iminothiazolines which might be formed by the action of bromoacetophenone on *s*-phenyl-*p*-tolylthiocarbamide, only 2-p-*tolylimino*-3:4-*diphenyl*-2:3-*thiazoline*,



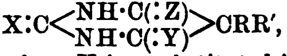
$$C_7H_7\cdot N\colon C<\begin{matrix}NPh\cdot CPh\\ S——CH\end{matrix},$$

could be isolated. It crystallises in white needles, m. p. 209°, and, when heated with carbon disulphide, yields 2-thio-3:4-diphenyl-2:3-thiazoline, m. p. 148°, together with *s*-di-*p*-tolylthiocarbamide, m. p. 176°. G. Y.

Preparation of 5:5-Dialkylbarbituric Acids. EMANUEL MERCK (D.R.-P. 177694).—Diethylbarbituric acids were formerly obtained by heating diethylmalonyl chloride with biuret when the group $CO\cdot NH_2$ was eliminated. It has now been found that in a similar manner the dialkylmalonyl chlorides react with the alkyl allophanates so that the group CO_2R is removed.

On heating a mixture of ethyl allophanate and diethylmalonyl chloride at 115—120°, hydrogen and ethyl chlorides and carbon dioxide are evolved and the residue contains diethylbarbituric acid. G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. OTTO WOLFES (D.R.-P. 175592).—The iminopyrimidines having the general formula



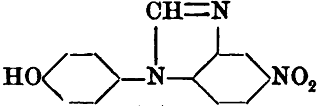
$$X\colon C<\begin{matrix}NH\cdot C(\colon Z)\\ NH\cdot C(\colon Y)\end{matrix}>CRR',$$

where X, Y, and Z may be imino-groups or where X is a substituted imino-group, such as $\colon N\cdot CN$ or $\colon NMe$, are all converted by alkyl nitrites into the corresponding dialkylbarbituric acids.

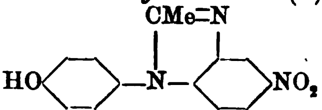
2-Imino-4:6-dioxy-5:5-diethylpyrimidine when heated in absolute alcohol with amyl nitrite yields diethylbarbituric acid.

The following compounds also give rise to the same dialkylbarbituric acid when similarly treated: 4-imino-2:6-dioxy-5:5-diethylprimidine, 2:4-di-imino-6-oxy-5:5-diethylpyrimidine and 2-methylimino-4:6-dioxy-5:5-diethylpyrimidine. G. T. M.

[Anhydro-Bases from 4′-Nitro-2′-amino-4-hydroxydiphenylamine.] D. MARON (D.R.-P. 175829).—The *methenyl* derivative (I.)



(I.)



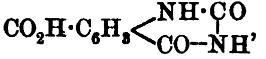
(II.)

of 4′-nitro-2′-amino-4-hydroxydiphenylamine is prepared by heating this substituted diamine with 25% formic acid and crystallising the product from alcohol, m. p. 267—268°.

The *ethenyl* derivative (II.) is obtained in a similar manner by the action of acetic anhydride, m. p. 187—188°. The *benzenyl* derivative produced by heating the nitroamino-compound with benzoyl chloride in xylene is crystallised from alcohol and melts at 259—260°. These compounds when heated with benzidine and sulphur at 220—240° yield sulphur dyes which give green and yellow shades on unmordanted cotton. G. T. M.

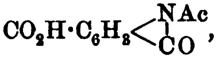
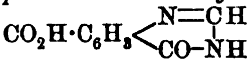
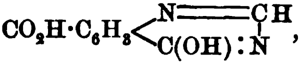
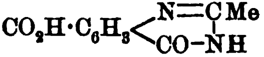
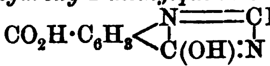
Quinazolines. XVII. Synthesis of Quinazolinecarboxylic Acids from 4-Amino*iso*phthalic Acid and from Aminoterephthalic Acid. MARSTON T. BOGERT, JOHN DAVID WIGGIN, and J. EDWIN SINCLAIR (*J. Amer. Chem. Soc.*, 1907, **29**, 82—87. Compare Abstr., 1906, i, 988, and earlier abstracts).

—The only quinazolinecarboxylic acid described previously is the carbamidobenzoylcarboxylic acid (diketotetrahydroquinazoline-2-carboxylic acid),

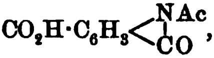


$$CO_2H\cdot C_6H_3\left<\begin{array}{l}NH\cdot CO\\ CO-NH\end{array}\right.,$$

obtained by Niementowski (Abstr., 1896, i, 578). In the present paper, a number of quinazolinecarboxylic acids are described which were prepared from *m*- and *p*-xylidines. The xylidines were acetylated, the methyl groups oxidised to carboxyl groups, the resulting acetylaminophthalic acids converted into acetylanthranilcarboxylic acids by the action of acetic anhydride, and from these the quinazolines were obtained by the action of primary amines. The nonalkylated quinazolines were prepared by the action of formamide on the ammonium aminophthalates. The quinazolinecarboxylic acids are colourless, crystalline substances which usually melt and decompose above 300°, are sparingly soluble in water, insoluble or nearly so in ether, benzene, chloroform, carbon tetrachloride, or acetone, and soluble in alcohol or aqueous alkali hydroxides; they form salts with the heavy metals. The following substances are described.

Acetylanthranil-5-*carboxylic acid*,  $CO_2H\cdot C_6H_3\left<\begin{array}{l}NAc\\ CO\end{array}\right.$, m. p. 264°, minute, colourless crystals. 4-*Ketodihydroquinazoline*-6-*carboxylic acid* (4-*hydroxyquinazoline*-6-*carboxylic acid*),  $CO_2H\cdot C_6H_3\left<\begin{array}{l}N{=}CH\\ CO-NH\end{array}\right.$ or  $CO_2H\cdot C_6H_3\left<\begin{array}{l}N{=\!=}CH\\ C(OH):N\end{array}\right.$, small, pale-yellow crystals. 4-*Keto*-2-*methyldihydroquinazoline*-6-*carboxylic acid* (4-*hydroxy*-2-*methylquinazolinecarboxylic acid*),  $CO_2H\cdot C_6H_3\left<\begin{array}{l}N{=}CMe\\ CO-NH\end{array}\right.$ or  $CO_2H\cdot C_6H_3\left<\begin{array}{l}N{=\!=}CMe\\ C(OH):N\end{array}\right.$, 4-*keto*-2 : 3-*dimethyldihydroquinazoline*-6-*carboxylic acid*, and 4-*keto*-3-*phenyl*-2-*methyldihydroquinazoline*-6-*carboxylic acid* form minute, colourless needles.

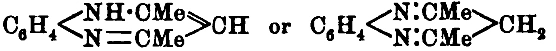
2-*Acetylaminoterephthalic acid*, $NHAc\cdot C_6H_3(CO_2H)_2$, crystallises in colourless, feathery needles and, on hydrolysis with sulphuric acid, yields 2-aminoterephthalic acid together with another *substance*, m. p. 59°, which forms colourless, pearly scales, and on successive treatment with acetic anhydride and ammonia is converted into a *compound*, m. p. 92°, which crystallises in colourless, silky needles.



Acetylanthranil-4-carboxylic acid, $CO_2H\cdot C_6H_3{<}\begin{matrix}NAc\\ |\\ CO\end{matrix}$, m. p. above 300°, minute, colourless crystals. 4-*Ketodihydroquinazoline-7-carboxylic acid* (4-*hydroxyquinazoline-7-carboxylic acid*) colourless, microscopic crystals. 4-*Keto-2-methyldihydroquinazoline-7-carboxylic acid* (4-*hydroxy-2-methylquinazoline-7-carboxylic acid*), resembles the isomeric 6-carboxylic acid. 4-*Keto-2 : 3-dimethyldihydroquinazoline-7-carboxylic acid*, m. p. 298°, small, colourless prisms. 4-*Keto-3-phenyl-2-methyldihydroquinazoline-7-carboxylic acid* forms small, colourless crystals and decomposes above 300° without melting. E. G.

Seven-Membered Rings from β-Diketones and Ortho-diamines. JOHANNES THIELE and GERHARD STEIMMIG (*Ber.*, 1907, **40**, 955—957).—Acetylacetone readily condenses with *o*-diamines in acid solution, yielding bases free from oxygen; the hydrochlorides of these form dark violet crystals, whereas the bases themselves are colourless. Benzoylacetone reacts less readily than acetylacetone. The bases appear to be formed by the elimination of 2 molecules of water from molecular proportions of the ketone and amine.

Acetylacetone and *o*-phenylenediamine dissolved in a mixture of alcohol and acetic acid yield a *base*, $C_{11}H_{12}N_2$, which can be isolated in the form of its *hydrochloride*, $C_{11}H_{12}N_2,HCl,2H_2O$, when diluted with water and mixed with concentrated hydrochloric acid. The salt crystallises in practically black needles, loses its water of crystallisation when kept in a desiccator, dissolves fairly readily in water, but when boiled with this solvent yields acetone and methylbenziminazole. With phenylhydrazine it yields the *o*-diamine and phenyldimethylpyrazole. The salt dissolves in fuming hydrochloric or concentrated sulphuric acid, yielding a colourless solution, which turns purple on the addition of water. When hydrogen chloride is led into a suspension of the violet salt in hydrochloric acid, a colourless, crystalline salt (+2HCl ?) is formed, but this immediately turns violet when filtered. The base crystallises from ether in colourless plates, m. p. 131—132°, and is more stable than the salts.

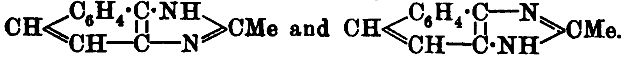


The formula $C_6H_4{<}\begin{matrix}NH\cdot CMe\\ N{=}CMe\end{matrix}{>}CH$ or $C_6H_4{<}\begin{matrix}N{:}CMe\\ N{:}CMe\end{matrix}{>}CH_2$ is suggested, and the compound is undoubtedly a pseudo-base.

The *hydrochloride* of the product from benzoylacetone and *o*-phenylenediamine has the composition $C_{16}H_{14}N_2,HCl,3H_2O$, and when boiled with water yields methylbenziminazole and acetophenone together with phenylbenziminazole and acetone. The *base* melts at 87—88°. J. J. S.

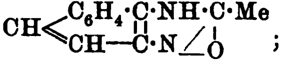
Tautomerism of Benziminazoles. OTTO FISCHER (*J. pr. Chem.*, 1907, [ii], **75**, 88—95. Compare Abstr., 1906, i, 895).—The

N-hydrogen atom in 2-methylbenziminazole is assumed by the author vibrate between the two nitrogen atoms; the same view should also apply to the corresponding naphthalene compound, but a second isomeric 2-methylnaphthiminazole, always, however, with a mol. of water of crystallisation, has been described by Meldola, Eyre, and Lane (Trans., 1903, 1185), the isomerism being represented thus:



$$CH{<}\genfrac{}{}{0pt}{}{C_6H_4\cdot C\cdot NH}{CH—C—N}{>}CMe \text{ and } CH{<}\genfrac{}{}{0pt}{}{C_6H_4\cdot C—N}{CH—C\cdot NH}{>}CMe.$$

The anhydrous isomeride known as Prager's base (Abstr., 1885, 1239) is shown to be 2-methyl-α-naphthiminazole (Fischer, Abstr., 1901, i, 414), and the isomeride containing the mol. of water of crystallisation is really 2-methyl-α-naphthiminazole oxide,



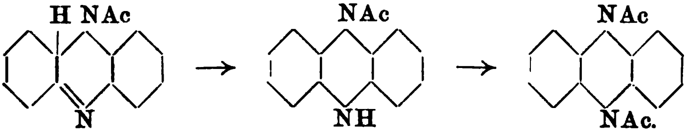
$$CH{<}\genfrac{}{}{0pt}{}{C_6H_4\cdot C\cdot NH\cdot C\cdot Me}{CH—C\cdot N\angle O};$$

this statement is supported by analysis and also by the fact that on reduction, such as distilling a mixture of it with iron powder, 2-methyl-α-naphthiminazole is obtained.

The action of methyl iodide on the isomeric 1 : 2 : 5- and 1 : 2 : 6-trimethylbenziminazoles has again been studied with the object of preparing two isomeric 1 : 2 : 3 : 6-tetramethylbenziminazolium iodides, but only one, m. p. 167—168° (Fischer and Rigand, Abstr., 1902, i, 399), was obtained. The author therefore concludes that in both cases the labile iodide, $C_6H_3Me{<}\genfrac{}{}{0pt}{}{NMe}{NMe}{>}C{<}\genfrac{}{}{0pt}{}{Me}{I}$, is first formed, which then passes into the stable form, m. p. 167—168°.

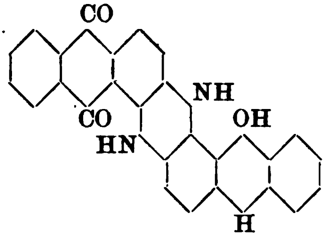
W. H. G.

Mono- and Di-acetyldihydrophenazines. NADEZDY STSCHERBINA (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 613—615).—The action of acetic anhydride on dihydrophenazine in the cold yields the same monoacetyldihydrophenazine as was obtained by Tichwinsky and Wolochowitsch (Abstr., 1905, i, 383) at a high temperature (compare Schaposchnikoff, Abstr., 1905, i, 840). The asymmetrica formula for dihydrophenazine is hence confirmed. On boiling the monoacetyl derivative with excess of acetic anhydride, it is converted into the diacetyl compound, m. p. 180°; it is concluded that the monoacetyl derivative undergoes molecular rearrangement before further acetylation occurs:

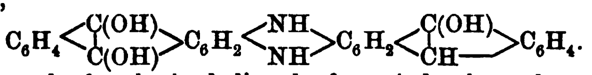


T. H. P.

Hydroazines. MICHAEL M. TICHWINSKY (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 615—620. Compare preceding abstract).—The author discusses the relation between the hydroazines and azines with especial reference to the work of Schaposchnikoff (Abstr., 1905, i, 840) and of Hinsberg (Abstr , 1902, i, 238). He disagrees with the former author's quinone formula for the azines. T. H. P.



Indanthrene and Flavanthrene. VII. Products of Reduction of Indanthrene. ROLAND SCHOLL and PH. STEGMÜLLER (*Ber.*, 1907, 40, 924—933. Compare Abstr., 1904, i, 109, 110; this vol., 255, 256, 257).—*N*-Dihydroanthraquinoneanthraquinolazine (this vol., i, 256) is very easily oxidised to indanthrene; if heated with 28% sodium hydroxide for ten hours at 220—230°, or in an atmosphere of carbon dioxide at 250°, for 1 molecule converted into indanthrene there is another converted into a compound $C_{28}H_{16}O_3N_2$. Its constitution was established thus: it is converted into an azine by oxidation and is therefore a *N*-dihydroazine, it can be reduced with hyposulphite showing it to contain an unaltered anthraquinone complex, and as it gives a sodium salt it is 1 : 2 : 1′ : 2′-N-*dihydroanthraquinone-anthranolazine*. It is a brownish-red powder which does not melt at 360°, its *hydrochloride* is blue, the *mono-acetate*, $C_{30}H_{18}O_4N_2$, is reddish-brown. 1 : 2 : 1′ : 2′-*Anthraquinone-anthranolazine*, $C_{28}H_{14}O_3N_2$, is obtained as a violet-brown powder by the oxidation of the corresponding dihydroazine with air or sodium hypochlorite. Reduction of the dihydroazine with sodium hyposulphite at 70° yields 1 : 2 : 1′ : 2′-N-*dihydroanthraquinolanthranolazine*,

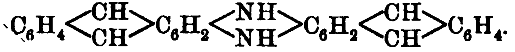


$$C_6H_4{<}\begin{matrix}C(OH)\\ |\\ C(OH)\end{matrix}{>}C_6H_2{<}\begin{matrix}NH\\ NH\end{matrix}{>}C_6H_2{<}\begin{matrix}C(OH)\\ |\\ CH\text{——}\end{matrix}{>}C_6H_4.$$

This may also be obtained directly from indanthrene by reduction with hyposulphite and serves as the most convenient source for *N*-dihydroanthraquinone-anthranolazine; the method of preparation and separation from anthranoneazine (Abstr., 1904, i, 111) is described in detail. The *triacetate* (?) is a brown powder, m. p. 240—243°.

W. R.

Indanthrene and Flavanthrene. VIII. Products of Reduction of Indanthrene. ROLAND SCHOLL [with HANS BERBLINGER and A. KÜNZEL] (*Ber.*, 1907, 40, 933—939. Compare preceding abstract).—Distillation of indanthrene with zinc dust yields anthrazine, but digestion with zinc dust and sodium hydroxide gives a compound, $C_{28}H_{18}N_2$, containing two hydrogen atoms more in the molecule than anthrazine. It crystallises in red aggregates having a metallic lustre, and is converted into the yellow anthrazine on heating at 360°. It is, therefore, N-dihydro-1 : 2 : 1′ : 2′-anthrazine,



$$C_6H_4{<}\begin{matrix}CH\\ CH\end{matrix}{>}C_6H_2{<}\begin{matrix}NH\\ NH\end{matrix}{>}C_6H_2{<}\begin{matrix}CH\\ CH\end{matrix}{>}C_6H_4.$$

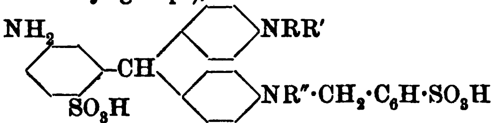
The author discusses the relationship of colour and constitution of the darker coloured dihydroazines and azines, and supports his conclusion that when chromogens containing more than one chromophore are reduced or altered in such a way that one chromophore remains whilst the other is converted into an auxochrome, a deepening in colour results. It is proposed to call such compounds *chromohydro*-compounds in distinction to the *leucohydro*-compounds.

Anthrazine sulphate, $C_{28}H_{16}N_2,H_2SO_4$, crystallises in brownish-red, microscopic needles; the *picrate*, $C_{28}H_{16}N_2(C_6H_3O_7N_3)_2$, in slender, red needles.

Octabromoanthrazine, $C_{28}H_8N_2Br_8$, obtained by heating the azine with bromine at 100° for six hours, is yellow. Boiling nitric acid probably gives a pentanitro-tetrahydroxyanthrazine. W. R.

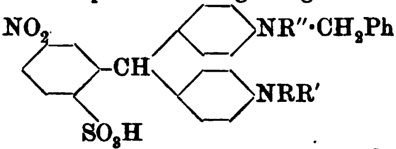
Preparation of Green Triphenylmethane Derivatives.

FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D.R.-P. 175825 and 175826).—The substituted triphenylmethanedisulphonic acids (where RR′ and R″ are alkyl groups),

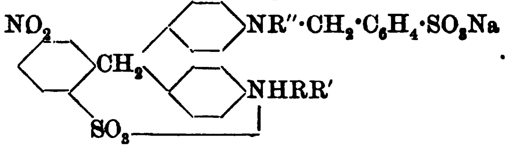


when diazotised and combined with salicylic acid give azo-derivatives which, on subsequent oxidation with lead peroxide furnish green colouring matters.

When the nitro-compounds having the general formula



are further sulphonated they yield disulphonic derivatives of the following type



G. T. M.

Synthesis of Tertiary Amidines [*iso*Diphenylcarbamidoacetanilide].

M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1907, **144**, 487—488).—By the action of amines, such as aniline, on a monosubstituted thiohydantoic acid, polysubstituted derivatives can be obtained. The iminic hydrogen is first replaced with loss of ammonia and then the acid is converted into the acid amide, the water liberated then reacting on the product with evolution of hydrogen sulphide and replacement of the sulphur atom by oxygen. It is possible to isolate the intermediate products.

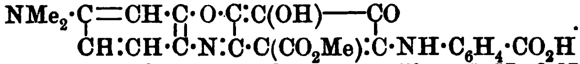
By the action of aniline on phenyl-ψ-thiohydantoic acid,

$$NHPh\cdot C(:NH)\cdot S\cdot CH_2\cdot CO_2H,$$

iso*diphenylcarbamidoacetanilide*, $NHPh\cdot C(:NPh)\cdot O\cdot CH_2\cdot CO\cdot NHPh$, is formed in small, white crystals, m. p. 289°. E. H.

Condensation of Gallocyanin Dyes with Amino-compounds.

EUGÈNE GRANDMOUGIN and ERNST BODMER (*J. pr. Chem.*, 1907, [ii], **75**, 199—200. Compare Abstr., 1906, i, 596; Nietzki and Bossi, Abstr., 1893, i, 44).—The *condensation* product of prune and *m*-aminobenzoic acid, formed in presence of sodium acetate in glacial acetic solution, separates in glistening, green crystals, is soluble in aqueous alkalis, and forms a greenish-blue chromium lake. It is considered to have the constitution

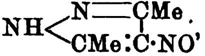


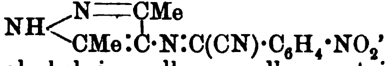
$$\begin{array}{l} NMe_2\cdot C{=}CH\cdot C\cdot O\cdot C{:}C(OH){-}CO \\ CH{:}CH\cdot C\cdot N{:}C\cdot C(CO_2Me){:}C\cdot NH\cdot C_6H_4\cdot CO_2H \end{array}.$$

The *condensation* product of prune and *m*-nitroaniline, $C_{22}H_{18}O_7N_4$, forms large, golden crystals, and is insoluble in aqueous alkalis. *Condensation* products have been formed also from prune with *p*-aminobenzoic acid, anthranilic acid, and *p*-nitroaniline, and from coreine with aniline, *m*-nitroaniline, and *m*-aminobenzoic acid. G. Y.

Preparation of Cyano-derivatives of Pyrimidine. EMANUEL MERCK (D.R.-P. 175795).—It is now found that the condensation of dicyanodiamide and the dialkylmalonic esters in presence of alkaline condensing agents takes place readily at 120° under pressure. Thus 2-cyanoimino-4 : 6-dioxy-5 : 5-diethylpyrimidine is obtained in good yield by heating at this temperature dicyanodiamide and ethyl diethylmalonate with alcoholic sodium ethoxide. G. T. M.

Condensations of Nitroso-compounds of the Pyrazole Series. FRANZ SACHS and PAUL ALSLEBEN (*Ber.*, 1907, **40**, 664—678).—It had previously been shown by Sachs and his pupils (Abstr., 1899, i, 883; 1900, i, 362; 1901, i, 229) that nitrosodimethylaniline, nitrosophenol, nitrosobenzene, and other nitroso-benzenoid derivatives react with methylene derivatives. A series of analogous condensations with tertiary nitroso-compounds of the pyrazole series is now described.

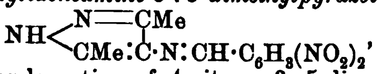
4-Nitroso-3 : 5-dimethylpyrazole,  $NH<\begin{array}{l}N{=}CMe\\ CMe{:}C\cdot NO\end{array}$, obtained by condensing hydrazine with *iso*nitrosoacetylacetone according to Wolff (Abstr., 1903, i, 203), was condensed with *p*-nitrobenzyl cyanide in the presence of ammonia or of piperidine; the resulting 4-p-*nitro-a-cyanobenzylideneamino*-3 : 5-*dimethylpyrazole*,



$$NH<\begin{array}{l}N{=}CMe\\ CMe{:}C\cdot N{:}C(CN)\cdot C_6H_4\cdot NO_2\end{array},$$

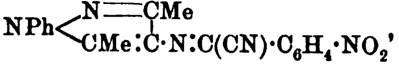
separates from alcohol in yellow needles containing $1H_2O$; the anhydrous compound has m. p. 229°. When dehydrated, the colour changes to an orange-red. Its solution in concentrated sulphuric acid is colourless.

4-op-*Dinitrobenzylideneamino*-3 : 5-*dimethylpyrazole*,

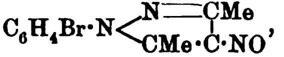


$$NH<\begin{array}{l}N{=}CMe\\ CMe{:}C\cdot N{:}CH\cdot C_6H_3(NO_2)_2\end{array},$$

obtained by the condensation of 4-nitroso-3 : 5-dimethylpyrazole with 2 : 4-dinitrotoluene, separates from methyl alcohol in yellowish-brown needles, which are transformed at 195° into a red modification, m. p. 212°. Its solution in concentrated sulphuric acid is yellowish-brown.

4-m-*Nitro-a-cyanobenzylideneamino*-1-*phenyl*-3 : 5 *dimethylpyrazole*,  $NPh<\begin{array}{l}N{=}CMe\\ CMe{:}C\cdot N{:}C(CN)\cdot C_6H_4\cdot NO_2\end{array}$, obtained by the condensation of nitrobenzyl cyanide with 4-nitroso-1-phenyl-3 : 5-dimethylpyrazole (Wolff, *loc. cit.*), separates from alcohol in glistening pyramids, m. p. 160°. It forms a very yellow solution with concentrated sulphuric acid.

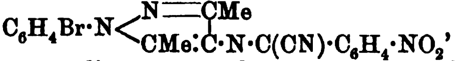
4-*Nitroso*-1-p-*bromophenyl*-3 : 5-*dimethylpyrazole*,



$$C_6H_4Br\cdot N\Big<\begin{array}{l}N{=\!=}CMe\\ CMe\cdot C\cdot NO\end{array},$$

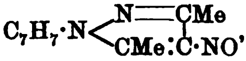
obtained from *p*-bromophenylhydrazine and *iso*nitrosoacetylacetone, separates from dilute alcohol in green needles, m. p. 122°; its solution in concentrated sulphuric acid is ruby-red.

4-p-*Nitro*-a-*cyanobenzylideneamino*-1-p-*bromophenyl*-3 : 5-*dimethylpyrazole*,



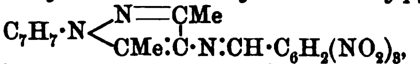
$C_6H_4Br\cdot N\Big<\begin{array}{l}N{=\!=}CMe\\ CMe\!:\!C\cdot N\cdot C(CN)\cdot C_6H_4\cdot NO_2\end{array}$, obtained by condensing the preceding compound with *p*-nitrobenzyl cyanide, separates from a mixture of chloroform and methyl alcohol in fan-shaped needles, m. p. 218·5°. Its solution in concentrated sulphuric acid is yellow.

4-*Nitroso*-1-p-*tolyl*-3 : 5-*dimethylpyrazole*,



$C_7H_7\cdot N\Big<\begin{array}{l}N{=\!=}CMe\\ CMe\!:\!C\cdot NO\end{array}$, obtained from *p*-tolylhydrazine and *iso*nitrosoacetylacetone, separates from acetic acid in glistening, emerald-green needles, m. p. 109·5°. Its solution in concentrated sulphuric acid is cherry-red.

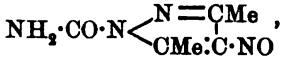
4-oo′p-*Trinitrobenzylideneamino*-1-*tolyl*-3 : 5-*dimethylpyrazole*,



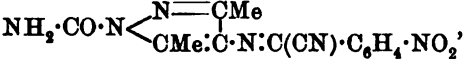
$$C_7H_7\cdot N\Big<\begin{array}{l}N{=\!=}CMe\\ CMe\!:\!C\cdot N\!:\!CH\cdot C_6H_2(NO_2)_3\end{array},$$

obtained from the preceding compound and 2 : 4 : 6-trinitrotoluene, separates from toluene in silky, orange-coloured needles, m. p. 235°, its solution in sulphuric acid is yellow. It is very stable towards dilute acid.

4-*Nitroso*-1-*carbamyl*-3 : 5-*dimethylpyrazole*,



$NH_2\cdot CO\cdot N\Big<\begin{array}{l}N{=\!=}CMe\\ CMe\!:\!C\cdot NO\end{array}$, obtained by the action of a mixture of semicarbazide hydrochloride and sodium acetate on *iso*nitrosoacetylacetone, crystallises from benzene in glistening, green needles, m. p. 130° (decomp.). When boiled with much water it forms a blue solution. Its solution in concentrated sulphuric acid is yellowish-brown; with alkalis it forms red salts. When condensed with *p*-nitrobenzyl cyanide, it forms 4-*p*-*nitro*-a-*cyanobenzylideneamino*-1-*carbamyl*-3 : 5-*dimethylpyrazole*,



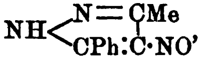
$$NH_2\cdot CO\cdot N\Big<\begin{array}{l}N{=\!=}CMe\\ CMe\!:\!C\cdot N\!:\!C(CN)\cdot C_6H_4\cdot NO_2\end{array},$$

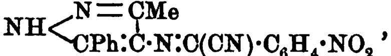
which crystallises from acetic acid in glistening, orange-coloured needles, m. p. 227°. Its solution in concentrated sulphuric acid is slightly yellow.

3-iso*Nitrosoacetylacetonesemicarbazone*,

$$NH_2\cdot CO\cdot NH\cdot N\!:\!CMe\cdot CAc\!:\!N\cdot OH,$$

obtained together with 4-nitroso-1-carbamyl-3 : 5-dimethylpyrazole by the action of semicarbazide on *iso*nitrosoacetylacetone, crystallises from glacial acetic acid in yellow needles, m. p. 192·5°. Its solution in concentrated sulphuric acid is faintly yellow, and it forms yellow salts with alkalis.

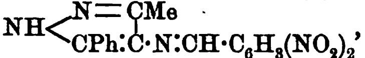
4-*Nitroso*-5-*phenyl*-3-*methylpyrazole*,  $\mathrm{NH}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CPh{:}C{\cdot}NO}\end{array}$, obtained by the action of hydrazine on *iso*nitrosobenzoylacetone, crystallises from dilute alcohol in dark green, serrated needles, m. p. 153° (decomp.). It forms red salts with alkalis. Its solution in concentrated sulphuric acid is dark red. When condensed with *p*-nitrobenzyl cyanide, it forms 4-m-*nitro-a-cyanobenzylideneamino*-5-*phenyl*-3-*methylpyrazole*,



$$\mathrm{NH}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CPh{:}C{\cdot}N{:}C(CN){\cdot}C_6H_4{\cdot}NO_2}\end{array},$$

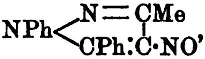
which crystallises from glacial acetic acid in bright red, rhombic plates, m. p. 136°. Its alkali salts are purple. It forms a red solution with concentrated sulphuric acid.

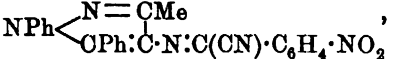
4-op-*Dinitrobenzylideneamino*-5-*phenyl*-3-*methylpyrazole*,



$$\mathrm{NH}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CPh{:}C{\cdot}N{:}CH{\cdot}C_6H_3(NO_2)_2}\end{array},$$

prepared by the condensation of 4-nitroso-5-phenyl-3-methylpyrazole with *op*-dinitrotoluene, crystallises from glacial acetic acid in yellowish-red pyramids, m. p. 240°. Its solution in concentrated sulphuric acid is yellowish-brown. Its alkali salts are dark red.

4-*Nitroso*-1 : 5-*diphenyl*-3-*methylpyrazole*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CPh{:}C{\cdot}NO}\end{array}$, obtained from phenylhydrazine and *iso*nitrosobenzoylacetone, separates from dilute acetic acid in bright green, rhombic plates, m. p. 137·5°. Its solution in concentrated sulphuric acid is dark red. When condensed with *p*-nitrobenzyl cyanide, it forms 4-p-*nitro-a-cyanobenzylideneamino*-1 : 5-*diphenyl*-3-*methylpyrazole*,

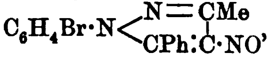


$$\mathrm{NPh}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CPh{:}C{\cdot}N{:}C(CN){\cdot}C_6H_4{\cdot}NO_2}\end{array},$$

which separates from alcohol in brick-red needles or in hexagonal prisms, m. p. 156°. Its solution in concentrated sulphuric acid is bright yellow.

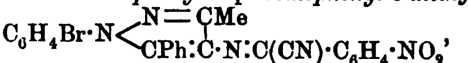
The azoxy-derivative of 4-*nitroso*-1 : 5-*diphenyl*-3-*methylpyrazole*, $C_{32}H_{26}ON_6$, obtained by the addition of a few drops of sodium hydroxide to a boiling alcoholic solution of the nitrosopyrazole, separates from a mixture of chloroform and alcohol in glistening, serrated, bright brown leaflets, m. p. 211°.

4-*Nitroso*-5-*phenyl*-1-p-*bromophenyl*-3-*methylpyrazole*,



$$\mathrm{C_6H_4Br{\cdot}N}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CPh{:}C{\cdot}NO}\end{array},$$

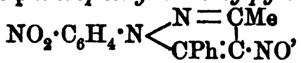
crystallises from alcohol in glistening, bright green, tetragonal plates, m. p. 130°. Its solution in concentrated sulphuric acid is dark brown. When condensed with *p*-nitrobenzyl cyanide, it forms 4-p-4-*nitro-a-cyanobenzylideneamino*-5-*phenyl*-1-p-*bromophenyl*-3-*methylpyrazole*,



$$\mathrm{C_6H_4Br{\cdot}N}<\begin{array}{l}\mathrm{N{=}CMe}\\ \mathrm{CPh{:}C{\cdot}N{:}C(CN){\cdot}C_6H_4{\cdot}NO_2}\end{array},$$

which separates from glacial acetic acid in cinnabar-red, rhombic crystals, m. p. 194°. It forms a yellow solution with concentrated sulphuric acid.

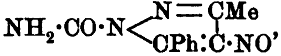
4-*Nitroso*-5-*phenyl*-1-p-*nitrophenyl*-3-*methylpyrazole*,



$$NO_2\cdot C_6H_4\cdot N\left<\begin{array}{l} N{=}CMe \\ \quad\;\; | \\ CPh{:}C\cdot NO \end{array}\right.,$$

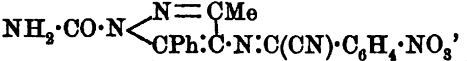
obtained by the condensation of *p*-nitrophenylhydrazine with *iso*nitrosobenzoylacetone, separates from glacial acetic acid in olive-green, rhombic crystals, m. p. 135°. Its solution in concentrated sulphuric acid has a claret tint. In addition to the pyrazole, the condensation in question leads to the formation of 3-iso*nitrosobenzoylacetone*-p-*nitrophenylhydrazone*, $NO_2\cdot C_6H_4\cdot NH\cdot N{:}CMe\cdot CBz{:}N\cdot OH$, which separates from methyl alcohol in hexagonal, glistening, dark yellow pyramids, m. p. 211° (decomp.). Its solution in concentrated sulphuric acid is red.

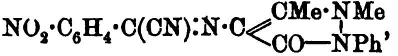
4-*Nitroso*-1-*carbamyl*-5-*phenyl*-3-*methylpyrazole*,



$$NH_2\cdot CO\cdot N\left<\begin{array}{l} N{=}CMe \\ \quad\;\; | \\ CPh{:}C\cdot NO \end{array}\right.,$$

obtained by the action of semicarbazide on *iso*nitrosobenzoylacetone, separates from acetic acid in green needles, m. p. 128° (decomp.). Its solution in concentrated sulphuric acid is ruby-red.

4-p-*Nitro-a-cyanobenzylideneamino*-1-*carbamyl*-5-*phenyl*-3-*methylpyrazole*,  $NH_2\cdot CO\cdot N\left<\begin{array}{l} N{=}CMe \\ \quad\;\; | \\ CPh{:}C\cdot N{:}C(CN)\cdot C_6H_4\cdot NO_2 \end{array}\right.$, obtained in the usual manner, separates from alcohol in cinnabar-red needles, m. p. 235°. Its solution in concentrated sulphuric acid is wine-red.

4-p-*Nitro-a-cyanobenzylideneamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone*,  $NO_2\cdot C_6H_4\cdot C(CN){:}N\cdot C\left<\begin{array}{l} CMe\cdot NMe \\ \qquad\quad | \\ CO{-}NPh \end{array}\right.$, obtained by the condensation of nitrosoantipyrine with *p*-nitrobenzyl cyanide, separates from alcohol in glistening, yellowish-red leaflets, m. p. 270°. Its solution in concentrated sulphuric acid is colourless. A. McK.

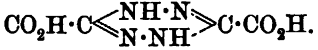
Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXIII. Constitution of *s*-Dihydrotetrazines.

ROBERT STOLLE (*J. pr. Chem.*, 1907, [ii], 75, 94—98. Compare Abstr., 1906, i, 709).—Polemical. The author contends that the arguments employed by Bülow (Abstr., 1906, i, 905) in support of his proposition that *s*-dihydrotetrazine is really 1-amino-3 : 4-triazole are not conclusive and that the constitution of this compound is still unsettled. W. H. G.

So-called Trisbisdiazomethanetetracarboxylic Acid and the Related Bisdiazomethane.

THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, 40, 815—837. Compare Abstr., 1906, i, 939; this vol., i, 21; Curtius and Lang, Abstr., 1889, 369; Curtius and Thompson, Abstr., 1906, i, 404, 940; Hantzsch and Silberrad, Abstr., 1900, i, 261; Silberrad, Trans., 1900, 77, 1185).—The authors have repeated Hantzsch and Silberrad's investigation of Curtius and Lang's tridiazoacetic acid (bisdiazoacetic acid) and its decomposition products. The conversion of trisbisdiazomethane tetracarboxylic acid into bisdiazomethane has been studied quantitatively and the results obtained found to agree with the empirical formula, $C_2H_3N_4{\cdot}CO_2H,\frac{1}{2}H_2O$, for the supposed tetracarboxylic acid, which is shown now to be identical with *C*-aminotriazolecarboxylic acid (Thiele and Manchot, Abstr., 1899, i, 167); bisdiazomethane formulated by Hantzsch and Silberrad as 3 : 6-dihydro-1 : 2 : 4 : 5-tetrazine being identical with *C*-aminotriazole.

The substance termed trimethinetriazoimide by Curtius and Lang, or *N*-dihydrotetrazine, $\mathrm{CH}{<}\substack{\mathrm{NH\cdot N}\\ \mathrm{N\cdot NH}}{>}\mathrm{CH}$, by Hantzsch and Silberrad, is considered by Bülow (Abstr., 1906, i, 905; this vol., i, 99) to be *N*-aminotriazole, $\mathrm{NH_2{\cdot}N}{<}\substack{\mathrm{CH{:}N}\\ \mathrm{CH{:}N}}$; from this it follows that the action of potassium hydroxide on bisdiazoacetic acid leads to the simultaneous formation of *C*-aminotriazolecarboxylic acid and *N*-aminotriazoledicarboxylic acid, $\mathrm{NH_2{\cdot}N}{<}\substack{\mathrm{C(CO_2H){:}N}\\ \mathrm{C(CO_2H){:}N}}$, previously considered to be 1 : 4-dihydrotetrazine-3 : 6-dicarboxylic acid,



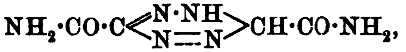
$$\mathrm{CO_2H{\cdot}C}{<}\substack{\mathrm{NH\cdot N}\\ \mathrm{N\cdot NH}}{>}\mathrm{C{\cdot}CO_2H}.$$

It is found now that Hantzsch and Silberrad's supposed dicarboxylic acid, m. p. 287°, is the *potassium hydrogen dicarboxylate*; when boiled with water, it decomposes forming *N*-aminotriazole. N-*Aminotriazoledicarboxylic acid*, m. p. 77°, is formed by the action of an excess of very dilute sulphuric acid on the potassium salt.

Contrary to Hantzsch and Silberrad's statement, *C*-aminotriazole (bisdiazomethane) is not converted into *N*-aminotriazole hydrochloride (dihydrotetrazine hydrochloride) by the action of boiling dilute hydrochloric acid. It is found that C-*aminotriazole hydrochloride* and *N*-aminotriazole hydrochloride melt at exactly the same temperature, 153°. The bases are distinguished by their behaviour with nitrous acid, *C*-aminotriazole being diazotised, whilst *N*-aminotriazole is converted into triazole.

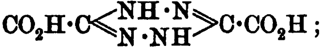
Dihydrotetrazine, $\mathrm{CH}{<}\substack{\mathrm{NH\cdot NH}\\ \mathrm{N{-\!\!-\!\!-}N}}{>}\mathrm{CH}$, formed by reduction of tetrazine with hydrogen sulphide (this vol., i, 262), crystallises in yellow prisms, m. p. 125—126°, and is readily oxidised by air, more completely by nitrous acid, forming tetrazine; the dihydrotetrazine is hydrolysed rapidly by sulphuric acid, forming hydrazine sulphate and formic acid, which is analogous to the formation of hydrazine and oxalic acid by the hydrolysis of bisdiazoacetic acid. As *N*-aminotriazoledicarboxylic acid is converted by the action of hot acids into *N*-aminotriazole, which is stable towards dilute acids, it cannot be formed as an intermediate product in the hydrolysis of bisdiazoacetic acid as supposed by Bülow (*loc. cit.*). When fused, dihydrotetrazine undergoes isomeric change into *N*-aminotriazole, which explains the formation of this substance by the action of heat on bisdiazoacetic acid.

Of the four possible dihydrotetrazines, that described above is the only one which has been prepared. Of derivatives of dihydrotetrazines, ψ-diazoacetamide is held to have the constitution,



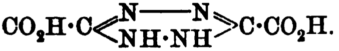
$$\mathrm{NH_2\cdot CO\cdot C}\left<\begin{matrix}\mathrm{N\cdot NH}\\ \mathrm{N{=}N}\end{matrix}\right>\mathrm{CH\cdot CO\cdot NH_2},$$

whilst the formation of bisdiazoacetic acid from ethyl *iso*diazoacetate points to its having the structure,



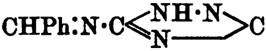
$$\mathrm{CO_2H\cdot C}\left<\begin{matrix}\mathrm{NH\cdot N}\\ \mathrm{N\cdot NH}\end{matrix}\right>\mathrm{C\cdot CO_2H};$$

it is possible that this is tautomeric with the structure,

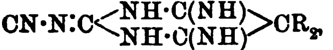


$$\mathrm{CO_2H\cdot C}\left<\begin{matrix}\mathrm{N{-}{-}N}\\ \mathrm{NH\cdot NH}\end{matrix}\right>\mathrm{C\cdot CO_2H}.$$

The condensation product of salicylaldehyde and bisdiazomethane, considered by Ruhemann (Trans., 1906, 89, 1268) to be a derivative of *C*-dihydrotetrazine, must be derived from *C*-aminotriazole. *Benzylidene-C-aminotriazole*, $\mathrm{CHPh{:}N\cdot C}\left<\begin{matrix}\mathrm{NH\cdot N}\\ \mathrm{N{-}{-}{-}{-}}\end{matrix}\right>\mathrm{CH}$, prepared by the action of benzaldehyde and pyridine on *C*-aminotriazole in absolute alcoholic solutions, forms a sparingly soluble, white, crystalline precipitate, m. p. 210°. G. Y.



Preparation of 4 : 6-Di-imino-5 : 5-dialkyl-2-cyanoiminopyrimidines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 175588 and 175589).—By the interaction of dialkylmalononitriles and dicyanodiamide in the presence of alkaline condensing agents, pyrimidine derivatives are produced which probably have the general formula $\mathrm{CN\cdot N{:}C}\left<\begin{matrix}\mathrm{NH\cdot C(NH)}\\ \mathrm{NH\cdot C(NH)}\end{matrix}\right>\mathrm{CR_2}$, where R is an alkyl group. These substances have the valuable property of being easily converted by hydrolytic agents into the technically important dialkylbarbituric acids. The condensation product from dicyanodiamide and diethylmalononitrile crystallises from boiling water in needles, m. p. 270°.



These condensations may be effected by prolonged warming on the water-bath, but the action is accelerated and the yield increased by heating at higher temperatures under pressure.

The foregoing condensation is thus carried out in alcoholic potash at 120°. G. T. M.

Reaction between Hydrogen Peroxide and Diphenylamine in Sulphuric Acid Solution. A. USCHAKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 959—962. Compare Abstr., 1906, i, 159).—Further study of the compound, m. p. 240°, obtained by the action of zinc dust on the compound $C_{60}H_{49}O_2N_5$ (*loc. cit.*), shows it to be diphenylbenzidine, $NHPh\cdot C_6H_4\cdot C_6H_4\cdot NHPh$, m. p. 242°; the best yield of the latter is obtained by gradually raising the temperature of the mixture of zinc dust and the compound in a combustion tube. When diphenylamine itself is heated with zinc dust in this way, no diphenylbenzidine is formed.

The two compounds obtained by the interaction of hydrogen peroxide and diphenylamine in presence of sulphuric acid must be regarded as condensation products of the compound,

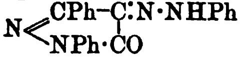
$OH\cdot C_6H_4\cdot NHPh$,

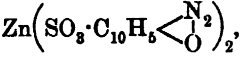
the sulphuric acid acting as condensing agent. The action of benzoyl chloride on these condensation products indicates that they contain hydroxyl groups.

The same compounds are obtained by the action of an electric current on a sulphuric acid solution of diphenylamine as by the action of hydrogen peroxide. T. H. P.

Action of Sodium Hyposulphite on Diazo-Salts. EUGÈNE GRANDMOUGIN (*Ber.*, 1907, 40, 858—859. Compare this vol., i, 263).—An alkaline solution of sodium hyposulphite reacts with the solution of a diazo-salt to displace the diazo-group by hydrogen. C. S.

[Azo-derivative of Anthranilic Acid.] FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 175828).—Anthranilic acid diazotised and introduced into a solution of sodium β-naphthol-6-sulphonate in sodium carbonate yields a reddish-bronze azo-compound which is soluble in water or concentrated sulphuric acid to a yellowish-red solution. Its lake has a vivid red colour and is extremely fast to light. G. T. M.

Constitution of Azo-derivatives of Ethyl Benzoylacetate. ANDRÉ WAHL (*Compt. rend.*, 1907, 144, 569—571).—Ethyl benzoylglyoxalate (this vol., i, 217) combines with phenylhydrazine in presence of alcohol or dilute acetic acid to furnish an *additive* product, $C_{17}H_{18}O_4N_2$, m. p. 89—90°, which crystallises from alcohol in colourless or faintly yellow needles, and rapidly decomposes even in the absence of air, producing a mixture of 4-phenylhydrazo-1 : 3-diphenyl-5-pyrazolone,  $N{<}\begin{array}{l}CPh{-}C{:}N\cdot NHPh\\ \qquad\;\;|\\ NPh\cdot CO\end{array}$ (Stierlin, Abstr., 1888, 1089), and ethyl benzoylglyoxalate-phenylhydrazone. The latter may also be obtained by the action of phenylhydrazine (1 mol.) on the ester dissolved in cold acetic acid. It is identical with Stierlin's (*loc. cit.*) ethyl benzeneazobenzoylacetate and must be represented by the formula $NHPh\cdot N{:}CBz\cdot CO_2Et$, since on treatment with acetic anhydride in presence of a drop of sulphuric acid, it yields an acetyl derivative, which on reduction with zinc and sulphuric acid furnishes acetanilide (compare Bülow and Hailer, Abstr., 1902, i, 325). These results indicate that the azo-derivatives of the benzoylacetic series have the phenylhydrazone structure. Bouveault and Wahl have shown (Abstr., 1904, i, 789) that when phenylhydrazine reacts with the acetylglyoxalates condensation takes place with the β- in place of the α-carbonyl group as in the present instance. T. A. H.

Preparation of the Sulphonic Acids of 1-Diazo-2-oxynaphthalene. KALLE & CO. (D.R.-P. 175593).—The orthoaminonaphtholsulphonic acids are not readily diazotised by the ordinary process, but when the normal salt of the sulphonic acid of 1-amino-β-naphthol is treated with zinc nitrite the diazo-oxynaphthalenesulphonic acid is obtained in the form of its zinc salt. The same result is produced when a mixture of a soluble zinc salt and an alkali nitrite is used, and when the free aminonaphtholsulphonic acids or the acid salts of the aminonaptholpolysulphonic acids are employed. When treated in this way, 1-amino-β-naphthol-4-sulphonic acid gives rise to *zinc* 1-*diazo*-2-*oxynaphthalene*-4-*sulphonate*,  $\mathrm{Zn}\left(\mathrm{SO_3 \cdot C_{10}H_5} < \overset{N_2}{\underset{O}{|}}\right)_2$, which crystallises from hot water in well-defined needles having a bronze lustre. G. T. M.

Sulphonation of Diazo-oxynaphthalene-4-sulphonic Acids. KALLE & Co. (D.R.-P. 176618 and 176620).—The diazo-oxynaphthalenesulphonic acids, prepared from the ortho-aminonaphtholsulphonic acids by the action of the nitrites of zinc, nickel, mercury, and other heavy metals, are remarkably stable diazo-derivatives which may be recrystallised and dried without undergoing any change. It has now been found that these diazo-compounds can actually be sulphonated.

1-Diazo-2-oxynaphthalene-4-sulphonic acid, when treated at 30—50° with fuming sulphuric acid containing about 6% of sulphuric trioxide, yields a soluble sulphonated product which can be salted out from aqueous solution as a pale yellow, crystalline precipitate. Similar sulphonated products are obtained from 1-diazo-2-oxynaphthalene-6-sulphonic acid and 2-diazo-1-oxynaphthalene-5-sulphonic acid.

G. T. M.

Nitration of Diazo-oxynaphthalenesulphonic Acids. KALLE & Co. (D.R.-P. 176619).—The diazo-oxynaphthalenesulphonic acids when dissolved or suspended in concentrated sulphuric acid are readily nitrated on the addition of either a nitrate or a mixture of nitric and sulphuric acids.

1-Diazo-2-oxynaphthalene 6-sulphonic acid when nitrated in this way furnishes a soluble, yellow, crystalline *nitro*-derivative which may be salted out from its aqueous solution. 2-Diazo-1-oxynaphthalene-5-sulphonic acid furnishes a similar *nitro*-derivative which may be recrystallised from dilute hydrochloric acid. G. T. M.

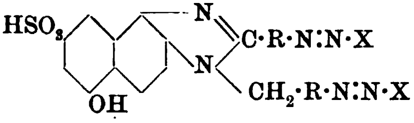
Preparation of Azo-derivatives of the Pyrazolone Group. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 176954).—*m*-Xylidine-*o*-sulphonic acid when diazotised and coupled with 1-*p*-sulphophenyl-3-methyl-5-pyrazolone furnishes a yellow dye, and similar compounds are obtained from 1-*p*-sulpho-*o*-tolyl-3-methyl 5-pyrazolone, 1-*p*-sulpho-*o*-tolyl-5-pyrazolone-3-carboxylic acid, and 1-phenyl-3-methyl-5-pyrazolone. These compounds are distinguished by their beautiful yellow colour and their fastness to light. G. T. M.

Formation of New Polyazo-dyes According to Hitherto Unknown Law. LUDWIG PAUL (*Zeitsch. angew. Chem.*, 1907, 20, 268—272).—It has hitherto been supposed that only when a benzene or naphthalene derivative contains so-called primary groups, such as the hydroxyl groups in resorcinol or 1-8-dihydroxynaphthalene, or a hydroxyl and an amino-group as in aminonaphthol, is it possible for 1 molecule of this compound to combine directly with more than 1 molecule of a diazo-compound to form polyazo-dyes. The author finds, however, that all monoazo-dyes derived from diazonaphthalene, diazonaphthols, or the sulphonic acids of these compounds are capable of combining directly with a further molecule of a diazo- or bisdiazo-compound; for example, 1-naphthionic acid-azonaphthalene-4-sulphonic acid combines with 1 molecule of *p*-nitrodiazobenzene to form a reddish-brown dye to which is assigned the formula

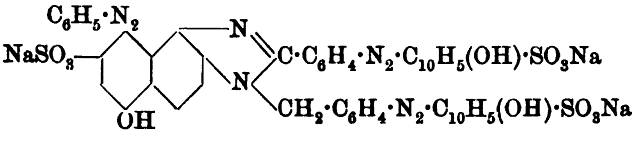
$$HSO_3{\cdot}C_{10}H_5(NH_2){\cdot}N{:}N{\cdot}C_{10}H_5(SO_3H){\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2.$$

By adding diazotised benzidine to 1-naphthionic acid-azonaphthalene-4-sulphonic acid, an intermediate condensation product is obtained, which condenses further with phenols, aromatic amines, and derivatives of these compounds to form dyes of various shades of red. In the same way, a considerable number of dyes of various colours have been obtained by coupling phenols, aromatic amines, and derivatives of these substances with the intermediate condensation products obtained by condensing diazotised benzidine with several monoazo-dyes derived from the sulphonic acids of diazonaphthalene and diazonaphthols. No analyses of the compounds obtained are given. W. H. G.

Preparation of Polyazo-derivatives. LEOPOLD CASSELLA & Co. (D.R.-P. 175666).—1 : 2-Diamino-5-hydroxynaphthalene-7-sulphonic acid condenses with two molecular proportions of a monoazo-compound containing an aldehydic group to furnish bisazo-colouring matters having the general formula , where R is a bivalent aromatic group and X an aminic or phenolic residue. These compounds when further condensed with a diazo-compound are substantive dyes for cotton which are extremely fast to light, acid, and scouring agents. The most useful substances from this point of view are those derived from *m*-diazobenzaldehyde and the naphtholsulphonic acids.



The azo-compound from diazotised *m*-aminobenzaldehyde and *β*-naphthol-6-sulphonic acid is condensed with 1 : 2-diamino-5-hydroxynaphthalene-7-sulphonic acid in hot dilute acetic acid solution, the ring formation being completed by further boiling with hydrochloric acid. The product is then collected, redissolved in aqueous sodium carbonate, and coupled with diazobenzene chloride; the resulting trisazo-compound is a red powder which dyes unmordanted cotton in yellowish-scarlet shades. In these condensations the *β*-naphthol-6-sulphonic acid may be replaced by other naphtholsulphonic acids and the aniline by other



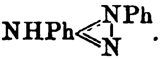
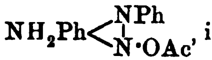
aromatic amines. A table of the dyes produced by these various combinations is given in the patent. G. T. M.

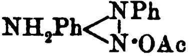
Isomeric Diazoaminobenzene. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 587—595).—If a primary aromatic base, such as aniline, is diazotised by means of sodium nitrite in presence of acetic acid instead of a mineral acid, orange-coloured spangles separate and the yellow solution obtained, which contains a nitrosoamine, exhibits the reactions of diazo-solutions, that is, it yields an azo-colouring matter with alkaline phenol or naphthol solution, whilst, when it is treated with cuprous chloride, molecular copper, or potassium iodide, decomposition and evolution of nitrogen occur. The formation of the nitrosoamine takes place according to the equation: $NH_2Ph + HNO_2 = NHPh \cdot NO + H_2O$, its reaction with phenols being expressed by $NHPh \cdot NO + C_6H_5 \cdot OH = NPh{:}N \cdot C_6H_4 \cdot OH + H_2O$, and its decomposition by $NHPh \cdot NO = Ph \cdot OH + N_2$.

When a solution of 7 grams of sodium nitrite in 30 c.c. of water is added to a mixture of 12 grams of glacial acetic acid, 18 grams of aniline, and 500 grams of water at the ordinary temperature, an *isomeride* of diazoaminobenzene separates as an orange-coloured precipitate, which gradually becomes crystalline and sometimes assumes a dark brown colour. In the latter form it has m. p. 91·5—93°, whilst when crystallised from alcohol it is deposited in leaflets, m. p. 81—94°. It is probably a mixture of substances or of different crystalline forms of the same substance, or possibly isomeric change occurs during the melting. It dissolves in glacial or 80% acetic acid, concentrated sulphuric acid, ether, benzene, chloroform, or alcohol, and partially in dilute hydrochloric (or sulphuric) acid giving a red solution, which, on heating, deposits aminoazobenzene hydrochloride: $C_{12}H_{11}N_3 + HCl = NPh{:}N \cdot C_6H_4 \cdot NH_2,HCl$. With alkaline β-naphthol solutions, its acetic acid solution yields a red azo-colouring matter at the ordinary temperature, whilst ordinary diazoaminobenzene gives a yellow azo-compound only on boiling. When treated in acetic acid solution with cuprous chloride, molecular copper, or potassium iodide, it decomposes completely at a moderate temperature, according to the equation:

$$C_{12}H_{11}N_3 + H_2O = PhOH + N_2 + NH_2Ph.$$

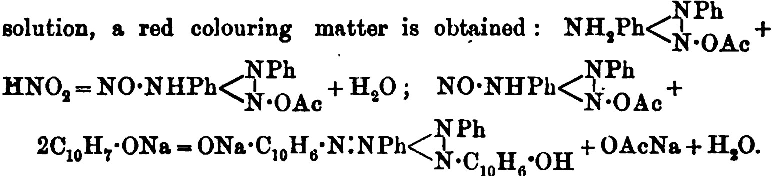
Cryoscopic measurements in acetic acid or nitrobenzene and ebullioscopic measurements in ether or carbon disulphide indicate the formula $C_{12}H_{11}N_3$. When reduced by means of zinc and hydrochloric acid, the compound is converted into phenylhydrazine and aniline.

The properties of the isomeric diazoaminobenzene are best represented by the formula  $NHPh\Big<\begin{matrix}NPh\\ |\\ N\end{matrix}$. On dissolving in acetic acid, a compound,  $NH_2Ph\Big<\begin{matrix}NPh\\ |\\ N \cdot OAc\end{matrix}$, is formed. The decomposition in presence of cuprous chloride, molecular copper, or potassium iodide is represented by the equation:



$$NH_2Ph\Big<\begin{matrix}NPh\\ |\\ N \cdot OAc\end{matrix} + H_2O = Ph \cdot OH + NH_2Ph + OAcH + N_2.$$

When the isomeric diazoaminobenzene is treated with excess of sodium nitrite in acid solution and subsequently with alkaline β-naphthol solution, a red colouring matter is obtained:



$$\mathrm{NH_2Ph}<\begin{matrix}\mathrm{NPh}\\ |\\ \mathrm{N{\cdot}OAc}\end{matrix} + \mathrm{HNO_2} = \mathrm{NO{\cdot}NHPh}<\begin{matrix}\mathrm{NPh}\\ |\\ \mathrm{N{\cdot}OAc}\end{matrix} + \mathrm{H_2O}; \quad \mathrm{NO{\cdot}NHPh}<\begin{matrix}\mathrm{NPh}\\ |\\ \mathrm{N{\cdot}OAc}\end{matrix} +$$

$$\mathrm{2C_{10}H_7{\cdot}ONa} = \mathrm{ONa{\cdot}C_{10}H_6{\cdot}N{:}NPh}<\begin{matrix}\mathrm{NPh}\\ |\\ \mathrm{N{\cdot}C_{10}H_6{\cdot}OH}\end{matrix} + \mathrm{OAcNa} + \mathrm{H_2O}.$$

In the preparation of the isomeric diazoaminobenzene and in the reactions described above, the acetic acid may be replaced by formic, lactic, tartaric, and other organic acids; but the stronger the acid used, the less the yield of the compound and the greater the instability of its solution in the acid. T. H. P.

Albumins of the White of Turkeys' Eggs. I. Crystalline Albumin.

WLADIMIR W. WORMS (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 597—607).—The white of turkeys' eggs contains, besides globulin, several albumins, one of which is crystalline, and may be isolated as follows. The egg-white is cut up, neutralised with 4% sulphuric acid solution and filtered through muslin, the solution being mixed with one-half its volume of saturated ammonium sulphate solution and filtered through a paper filter which is renewed from time to time. To the filtrate, sufficient saturated ammonium sulphate is added to render the liquid half saturated with the salt, and the globulin thus precipitated is removed by filtration after twenty-four hours. The filtrate is evaporated at the ordinary temperature and treated with saturated ammonium sulphate solution until a faint turbidity appears. The precipitate which gradually forms is filtered off when the deposition begins to slacken, and to the filtrate ammonium sulphate is again added until a slight turbidity appears. A sticky mass separates, which, when dissolved in one-fifth saturated ammonium sulphate solution and precipitated by a saturated solution of the salt, is deposited in almost colourless, slender needles and leaflets, readily soluble in water, but nearly insoluble in semi-saturated ammonium sulphate solution. Aqueous solutions of the albumin are slightly acid and give all the albumin reactions. It is completely coagulated by heating or by the addition of 95% alcohol. Its composition is represented by $C_{258}H_{422}O_{88}N_{68}S_8$ (compare Panormoff, Abstr., 1899, i, 655), and it has $[\alpha]_D^{20}$ − 34·9°. With hydrochloric acid, it gives a salt Alb.,4HCl. Although the albumin has the same composition and reactions as that obtained from hens' eggs (Panormoff, *loc. cit.*), it differs from the latter in specific rotation and in its property of being converted into a non-crystalline modification by treatment with water. T. H. P.

Presence of Phosphorus in Crystalline Egg-albumin.

Miss EDITH G. WILLCOCK and WILLIAM B. HARDY (*Proc. Camb. Phil. Soc.*, 1907, **14**, 119—120).—The presence of phosphorus in egg-albumin has only been mentioned by Osborne and Campbell (Abstr., 1900, i, 574), who consider it to be present as associated phosphate and not as a constituent of the protein molecule. The authors find that phosphorus is present as "organic" phosphorus, and that it is undoubtedly a constituent of crystalline egg-albumin, which, since it contains 0·13% of phosphorus, contains in 1 molecule 12 atoms of sulphur to each atom of phosphorus, thus giving the value 23,800 as the mol.-weight of this protein. W. H. G.

Action of Nitrous Acid on Egg-albumin. ZDENKO H. SKRAUP and KARL KAAS (*Annalen*, 1907, **351**, 379—389. Compare Paal, Abstr., 1896, i, 455; Schrötter, Abstr., 1898, i, 610).—In view of the interesting results obtained by treating casein with nitrous acid (Skraup and Hoernes, Abstr., 1906, i, 913), the authors have extended the reaction to other proteins. The present paper deals with the products obtained in this manner from crystalline egg-albumin (Kaas, Abstr., 1906, i, 777).

Deaminoalbumin, $C_{100}H_{160}O_{33}N_{25}S_{1·6}P_{1·6}$ (Schiff, Abstr., 1896, i, 632), is formed by the action of sodium nitrite and acetic acid on crystalline egg-albumin, $C_{100}H_{166}O_{3}N_{25}SP_{0·6}$; from analytical figures, it is concluded that the molecule of egg-albumin decomposes into two parts, the deaminoalbumin being formed from that which contains the more sulphur and phosphorus. Deaminoalbumin has a feeble acid reaction, gives with aqueous alkalis a yellow to brown, with α-naphthol and concentrated sulphuric acid a dark violet, or with thymol and sulphuric acid a yellowish-red solution, and behaves towards acids in the same manner as albumin. Whilst hydrolysis of egg-albumin leads to the formation of arginine and lysine, that of deaminoalbumin leads to the formation of arginine only. Histidine is not found in either of the products of hydrolysis. The lysine of egg-albumin is probably in that part of the molecule from which deaminoalbumin is not derived. G. Y.

A New Decomposition Product of Gliadin. THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, **18**, 123—126) —A crystalline substance was isolated from the products of acid hydrolysis of gliadin; a crystallographic study of its copper salt is given. It is probably a dipeptide, and yields proline and phenylalanine on further hydrolysis. W. D. H.

Ion-protein Compounds. IV. Properties of Caseinogen. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1907, **2**, 317—384).—Caseinogen (called casein in the paper) reddens litmus. A volumetric method of estimation is described, and the solubilities of the material in various salts estimated. The bulk of the paper deals with the physical chemistry (velocity of hydrolysis of caseinogen compounds, &c.) of the subject on the lines of the author's previous work. Proteins are regarded as amphoteric electrolytes. W. D. H.

Some Phenomena observed in the Peptic Digestion of Caseins. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1907, **29**, 223—230). —In a previous paper (Abstr., 1906, i, 391) it has been shown that the caseins of goat's milk and cow's milk are very similar, that the equivalent weight of the former is slightly lower than that of the latter, and that solutions of their salts have nearly the same electrical conductivity.

Experiments have now been made on the behaviour of the two caseins with pepsin and dilute hydrochloric acid at 38°. During the digestion, the casein does not dissolve completely, but leaves a light, flocculent residue of "pseudonuclein" which in appearance and quantity is characteristic of each casein. The casein of the goat's milk undergoes change more slowly than that of the cow's milk and the former leaves about 4·4% of "pseudonuclein," whilst the latter yields 12·8%. In the course of the digestion, the electrical conductivity and the total and free acidity vary regularly. Both acidity values are lower for the goat casein that for the cow casein.

After separating the "pseudonuclein," the filtrates were slowly evaporated and the residue dried at 100—105°. On weighing these residues, it was found that a considerable increase in weight had taken place owing to hydrolysis and combination with hydrochloric acid to form complex salts. The increase amounted to 31·5% in the case of the cow casein and to 36·4% in that of the goat casein. On redissolving these residues, the conductivities and total acidities of the solutions, when calculated on unit weight of solid present, were nearly the same for each casein. The chief difference in the two caseins therefore appears to be the amount of "pseudonuclein" obtainable. E. G.

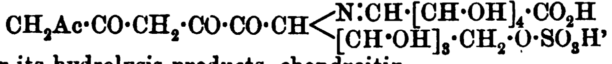
Relationship between Chlorophyll and Hæmoglobin. LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1907, 3, 320—322. Compare Abstr., 1905, i, 399, 500; 1906, i, 779).—Zaleski's hydrogenised hæmin is very like ordinary hæmin; on decomposition with hydrobromic acid in an acetic acid solution, it yields mesoporphyrin, a substance exactly like phylloporphyrin obtained from chlorophyll. The present research shows that by dissolving phylloporphyrin with warm glacial acetic acid saturated with sodium chloride, and warming it with some Mohr's salt dissolved in 50% acetic acid, on the water-bath, a brown pigment is obtained called phyllohæmin which spectroscopically is identical with hæmin. W. D. H.

New Reactions of Hæmatin. OTTO VON FÜRTH (*Annalen*, 1907, 351, 1—11. Compare Küster, Abstr., 1904, i, 357, 358).—I. *Action of Phenylhydrazine on Hæmin.*—Hæmin reacts with an excess of phenylhydrazine at the laboratory temperature with development of heat, evolution of ammonia, and formation of a *product* of the interaction of hæmin and aniline. This is obtained as a loose, brown powder containing nitrogen and iron in the proportion N : Fe = 7·9 : 1; after reduction with phosphonium iodide and hydriodic acid, D 2·0, in glacial acetic acid solution on the water-bath, it gives the characteristic reactions for hæmopyrrole. Hæmatoporphyrin does not react with phenylhydrazine.

II. *Action of Bromophenylhydrazine on Hæmin.*—*p*-Bromophenylhydrazine acts on hæmin at 50—60° with development of heat, evolution of gas, and formation of a brown, granular *product*, which is soluble in chloroform, and gives analytical results agreeing with the formula $C_{52}H_{45}O_6N_6Br_3Fe$. A similar product is formed by the action of *p*-bromophenylhydrazine on hæmatin. When reduced with phosphonium iodide and hydriodic acid in glacial acetic acid solution and distilled in a current of steam, it yields a *product* which gives the reactions characteristic of hæmopyrrole. The action of hydrogen bromide on the additive product of *p*-bromophenylhydrazine and hæmatin leads to the formation of hæmatoporphyrin and of a brown *product* which contains bromine and nitrogen in the proportion N : Br = 1 : 0·52, and is almost free from iron. G. Y.

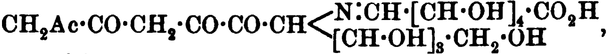
Oxidation of Nucleic Acid. II. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1907, **50**, 538—539. Compare Abstr., 1906, i, 915).—In order to obtain some knowledge of the nature of the carbohydrate obtainable from the nucleic acid of fish sperm, oxidation was carried out by means of nitric acid. The barium salt of an acid was obtained which in composition agrees with that of saccharic and mucic acids, but differs in its properties from both. It is suggested it may be Habermann's parasaccharic acid. W. D. H.

Chondroitin-sulphuric Acid. SIGMUND FRÄNKEL (*Annalen*, 1907, **351**, 344—353. Compare Mörner, Abstr., 1895, i, 254).—The results of an investigation of the products of the hydrolysis of chondroitin-sulphuric acid, with different strengths of sulphuric acid, support Schmiedeberg's formulæ for this substance,



$$CH_2Ac\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot CH<\begin{matrix}N\!:\!CH\cdot[CH\cdot OH]_4\cdot CO_2H\\ [CH\cdot OH]_3\cdot CH_2\cdot O\cdot SO_3H\end{matrix},$$

and for its hydrolysis products, chondroitin,



$$CH_2Ac\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot CH<\begin{matrix}N\!:\!CH\cdot[CH\cdot OH]_4\cdot CO_2H\\ [CH\cdot OH]_3\cdot CH_2\cdot OH\end{matrix},$$

and chondroisin,

$$CHO\cdot CH(N\!:\!CH\cdot[CH\cdot OH]_4\cdot CO_2H)\cdot[CH\cdot OH]_3\cdot CH_2\cdot OH$$

(*Arch. Exp. Pathol.*, 1891, **28**, 355), against the criticisms of Orgler and Neuberg (Abstr., 1903, i, 589), who failed to obtain any of the reactions for glycuronic acid.

Hydrolysis of copper chondroitin-sulphate by means of 70% sulphuric acid at the ordinary temperature leads in forty-eight hours to removal of the sulphuric acid and one acetyl group with formation of a *substance*, $C_{16}H_{23}O_{13}N,3H_2O$, which has an acid reaction, and has reducing properties after, but not before, being boiled with dilute sulphuric acid; the *barium* salt, $C_{16}H_{21}O_{13}NBa,5H_2O$, was analysed.

The two basic copper salts obtained on hydrolysis of copper chondroitin-sulphate with 10% sulphuric acid for ten hours, contain carbon and nitrogen in the proportion, C_{12}:N, and are derivatives of chondroisin.

The action of 70% sulphuric acid on copper chondroitin-sulphate at the laboratory temperature for four days, leads to the formation of a *substance*, $C_{10}H_{19}O_9N$, which reduces Fehling's solution, but does not form an insoluble phenylhydrazone.

When hydrolysed with 20% sulphuric acid in a current of hydrogen for twelve hours, copper chondroitin-sulphate yields an *aminoglycuronic* acid, $C_6H_{11}O_6N$, which is obtained as a white powder, and gives with orcinol and concentrated hydrochloric acid a violet coloration, becoming green on addition of ferric chloride; the green substance is extracted by amyl alcohol. G. Y.

Iodogorgonic Acid. Martin Henze (*Zeitsch. physiol. Chem.*, 1907, 51, 64—70).—Iodogorgonic acid, $C_9H_9O_3NI_2$, is an iodine compound prepared from Drechsel's gorgonin; it is identical with inactive di-iodotyrosine. Its method of preparation is described.
W. D. H.

Colloidal Nature of Albumose Solutions. Peter Rona and Leonor Michaelis (*Biochem. Zeitsch.*, 1907, 3, 109—115).—The albumoses contained in Riedel's peptone yield a flocculent precipitate with a mastic emulsion even in the absence of an electrolyte, but the precipitate is not obtained if the peptone solution is previously made slightly alkaline. The amount of mastic required in the case of peptone is much less than with albumins.

The method recommended for removing proteins is to make faintly alkaline, then add the mastic emulsion and finally acidify with acetic acid and add the electrolyte (magnesium sulphate). All the albumoses are not precipitated by this process, some 70% of the total peptone nitrogen is found in the filtrate, and the addition of phosphotungstic acid to the filtrate produces a heavy precipitate. To obtain the albumose from the mastic precipitate, the latter is dried and the mastic removed by extraction in a Soxhlet extractor with chloroform and the mixture of albumose and proteins carefully extracted with hot water. A series of experiments has shown that of 0·296 gram of peptone nitrogen originally present 0·062 gram is precipitated by mastic and 0·211 gram is not. The peptone not precipitated the first time cannot be precipitated by the addition of more protein and mastic to the filtrate. The concentration of the solution does not appear to affect the amount of albumose precipitated. The albumoses precipitated by the mastic are the "higher" albumoses which can be precipitated by ammonium sulphate; but the solution from the mastic precipitate also contains albumoses which can be salted out by means of ammonium sulphate. J. J. S.

Preparation of Solid Soluble Silver Salts in Combination with Colloids. Kalle & Co. (D.R.-P. 175794).—Colloidal silver carbonate is produced by precipitating silver protoalbinate or lysalbinate by mixing solutions of the sodium salt of one of these organic acids with silver nitrate, dissolving the precipitate in aqueous sodium carbonate, and dialysing the solution. On evaporating the dialysed solutions under reduced pressure at moderate temperatures a residue is obtained consisting of normal silver carbonate mixed with the colloidal alkali salt of the organic acid.

Colloidal silver phosphate is made by adding silver nitrite to a solution of sodium phosphate and sodium protoalbinate; the precipitate is dissolved by the addition of sodium phosphate and the clear solution dialysed.

Colloidal preparations containing a high percentage of silver chloride, bromide, and iodide are prepared similarly, the most stable of the series being the iodide. The preparation of this compound with sodium lysalbinate forms yellowish-brown granules containing 95% of silver iodide. G. T. M.

Plasteins. I. J. LUKOMNIK (*Beitr. chem. Physiol. Path.*, 1907, 9, 205—214).—Plastein is the name given to the precipitate which is the result of the action of rennet on "peptone" solutions. During dialysis against distilled water, the plastein-yielding material passes partly into the dialysate. Urea has no important action on the course of plastein formation, but it hinders their being "salted out" from solutions. The view taken of the precipitation of plastein is that it is due to a process of "salting out" which occurs during rennet action.

W. D. H.

Hydrolytic Decomposition Products of Caseoplastein. L. ROSENFELD (*Beitr. chem. Physiol. Path.*, 1907, 9, 215—231).—Five preparations of plastein from casein-peptone were made, and were found to be very similar in elementary composition. In comparison with caseinogen they have a high carbon and a low nitrogen percentage. Among their hydrolytic products, arginine, histidine, lysine, tyrosine, leucine, pyrrolidine-2-carboxylic acid, phenylalanine, and glutamic acid were identified. The following table contrasts the distribution of nitrogen in caseinogen and caseo-plastein.

	Caseinogen.	Caseoplastein.
Amino-nitrogen	9·48	3·12
Diamino-nitrogen	20·53	20·09
Nitrogen in unknown combination	69·99	76·79

W. D. H.

The Lecithin-like Substances from the Myocardium and from Striped Muscle. A. ERLANDSEN (*Zeitsch. physiol. Chem.*, 1907, 51, 71—155).—The wide distribution of phosphatides in the organism is confirmed. These, however, do not merely differ in the kind of fatty acid they contain, and may be classified into mono- and diaminomonophosphatides and diphosphatides. The monoaminomonophosphatides (the lecithin-kephalin group $N:P=1:1$) are the most abundant. The lecithin prepared from ox-flesh has the same formula as that prepared from egg-yolk ($C_{42}H_{80}O_9NP$); the two fatty acid radicles appear to belong to the linoleic acid series. The mono-aminodiphosphatides ($N:P=1:2$) are represented by *cuorin*, which was separated from the ox-heart. It contains two phosphoric acid radicles which are in part united to glycerol, three fatty acid radicles, and a basic substance which is not choline. Its empirical formula is $C_{71}H_{125}O_{21}NP_2$. It is characterised by its insolubility in alcohol, its auto-oxidisability, and the insolubility of its metallic compounds. Diamino-monophosphatides ($N:P=2:1$) are not regarded as existing free in the organism, but probably united to protein. After the proteins are coagulated by alcohol, the phosphatides can be extracted with ether. The cadmium compound of one from the heart had the formula $C_{40}H_{75}O_2N_2P,2CdCl_2$; this contains only one fatty acid radicle and two basic ones; the bases are, in part, different from choline. Thudichem's aminomyelin and sphengomyelin belong to this group. Diaminodiphosphatides ($N:P=2:2$) were isolated by Thudichem, but not found in the present research. No definite conclusions are reached respecting jecorin and protagon. The methods hitherto in use for estimating phosphatides, including the recent one of W. Kóch and Woods, are regarded as inaccurate. Precipitation by cadmium chloride also is not quantitative. W. D. H.

Inorganic Ferments and Organic Enzymes. Georg Bredig (*Chem. Zeit.*, 1907, **31**, 184—185).—A reply to Bokorny's criticisms (this vol., ii, 184); the latter's statement that organic enzymes once poisoned cannot be restored is disproved by the fact that both catalase and zymase which have been poisoned by hydrocyanic acid recover their activity on removal of the acid. P. H.

The Use of Antiseptics in Investigations on Enzymes. Alb. J. J. Vandevelde (*Biochem. Zeitschr.*, 1907, **3**, 315—319).—The difficulties of investigating enzyme action in the presence of most antiseptics are described. The experiments recorded with milk show that an admixture of iodoform and dimethyl ketone does not interfere with proteolytic and other enzyme activity, but yet ensures complete sterility. W. D. H.

Oxidation of Philothionic Hydrogen by Oxydases. Joseph de Rey-Pailhade (*Bull. Soc. chim.*, 1907, [iv], **1**, 165—167. Compare Abstr., 1906, i, 999).—When a solution of manganese chloride is mixed with white of egg diffused in water and sodium hydroxide is added, a solution is formed which becomes brown on exposure to air. The protein matter obtained by acidifying and then boiling the solution evolves hydrogen sulphide on the addition of sulphur. This property is still retained after heating the brown solution for two hours at 40—45°, but disappears after heating for four hours at the same temperature, this being due to the oxidation of the philothionic hydrogen. This oxidation does not occur in the absence of either manganese chloride or sodium hydroxide and probably indicates that philothionic hydrogen may be oxidised by the oxydase, which occurs in muscular tissue.

Philothion may be either an isomeride of non-philothionic protein or a hydrogenised product of ordinary protein, the hydrogen being obtained by the decomposition of water. T. A. H.

Organic Chemistry.

Abnormal Reactions, Especially in the Action of Alkyl Haloids on Salts. RUDOLF WEGSCHEIDER and ERICH FRANKL (*Monatsh.*, 1907, **28**, 79—114).—The formation of esters by the action of metallic salts on alkyl haloids takes place according to the equation: MA + AlkX = MX + AlkA (A = anion of organic acid, M = metal, X = halogen, Alk = alkyl); on the other hand, it is found frequently that the product obtained is not that of this normal reaction, but is a substance known to be formed by the action of an alcohol on the free organic acid. The normal reaction product is then to be obtained by the exclusion of water and alcohol, or sometimes by carrying out the reaction at low temperatures. Such cases occur in the action of methyl iodide on *o*-aldehydo-carboxylates, when ψ-esters may be formed (Abstr., 1892, 1208), and in the formation of β-alkyl hydrogen or dialkyl esters instead of α-alkyl hydrogen esters in the esterification of dibasic acids (Abstr., 1895, i, 520). Alongside of these must be placed the formation of free acids by the action of alkyl iodides on silver salts.

Whilst the formation of the free acid may be ascribed in a few cases to the hydrolysis of the normal reaction product by water or, in the esterification of sulphonic acids, by alcohol, it appears to result more generally from the action of the water or alcohol on the alkyl iodide, since not infrequently the normal product, which can be obtained only on exclusion of alcohol and water, is not hydrolysed by these to any marked extent, and the formation of the free acid is accompanied by that of alkyl ethers. This explanation, although satisfactory when the reacting substances are heated with water or alcohol for a long time at high temperatures, is insufficient when the reaction takes place at the ordinary temperature, as under these conditions alkyl haloids are hydrolysed by alcohol (Burke and Donnan, Trans., 1904, **85**, 587) or by water (Cain, Abstr., 1894, ii, 133) only very slowly. Certain results (Abstr., 1904, i, 249) have suggested that the amount of free acid formed is dependent on the nature of the organic acid; the action of methyl iodide on a number of organic silver salts has now been investigated and it is found that with silver acetate, phthalonate, camphorate, or benzoate the amount of free acid obtained is greater in presence of water and methyl alcohol than in that of the alcohol alone. Acetic acid is formed at the ordinary temperature or at 55° only in presence of water. On the other hand, 3-nitrophthalic acid is formed from the silver salt in approximately the same amount in methyl-alcoholic as in aqueous methyl-alcoholic solution. The conclusion is drawn that the action of methyl alcohol or water on methyl iodide is catalytically accelerated by the silver salt, the extent of the acceleration being dependent on the nature of the organic acid.

The formation of the free acid and the abnormal reactions to which it gives rise are discussed from a theoretical point of view. G. Y.

Identity of the Four Valencies of the Carbon Atom. LOUIS HENRY (*Bull. Acad roy. Belg.*, 1906, 722—731).—The author has compared the physical properties of the four nitromethanes and acetonitriles obtained by the successive replacement of the four atoms of hydrogen, one at a time, in methane by NO_2 and by CN respectively (compare Abstr., 1887, 711), and confirms his statement that each set of compounds consists of the same substance. The following physical constants are given: nitromethane, b. p. 101—102°/750—760 mm., D^{20}_{4} 1·13723—1·13782, n^{20}_{D} 1·39345—1·39358 (compare Brühl, Abstr., 1895, ii, 194), m. p. $-28·4°$ to $-28·5°$. Acetonitrile, b. p. 82·2—83°/747—764 mm., m. p. $-44°$ to $-46°$ (compare Schneider, Abstr., 1897, ii, 304), D^{20}_{4} 0·78614—0·78670, n^{20}_{D} 1·34420—1·34426 (compare Brühl, *loc. cit.*).

The coefficients of dilatation of the two compounds have been determined by De Heen, who finds for the following relation, $V_t = V_{10}(1 + a\tau + b\tau^2)$, where $\tau = t - 10$, that in the case of nitromethane between 10° and 100°, $a = 0·001147$ and $b = 0·000002356$, and for acetonitrile between 10° and 80°, $a = 0·0013$ and $b = 0·000003$. T. A. H.

Direct Dehydration of Dimethyl*iso*propylcarbinol. LOUIS HENRY (*Compt. rend.*, 1907, **144**, 552—554).—Dimethyl*iso*propylcarbinol was prepared by treating ethyl *iso*butyrate with magnesium methyl bromide. When heated with slight excess of acetic anhydride in presence of a little sulphuric acid, it is dehydrated, yielding a mixture of $\beta\gamma$-dimethyl-Δ^{α}-butylene, $CH_2{:}CMe{\cdot}CHMe_2$, b. p. 56—58°/767 mm., and $\beta\gamma$-dimethyl-Δ^{β}-butylene, $CMe_2{:}CMe_2$, b. p. 72—73°/767 mm. The same mixture of hydrocarbons is produced when dimethyl*iso*propyl bromide is heated with potassium acetate in presence of acetic acid, or when the haloid esters of *sec.*-pinacolyl alcohol are treated with alkalis (compare Delacre, Abstr., 1906, i, 476; 1907, i, 7). T. A. H.

Secondary C_7 and C_8 Alcohols. JOSEPH MUSET (*Bull. Acad. roy. Belg.*, 1906, 775—789. Compare Abstr., 1906, i, 723).—*Propyl*iso*propylcarbinol*, b. p. 141—142°/765 mm., D^{17} 0·821, n_D 1·41493, obtained by the action of *iso*butaldehyde on magnesium *n*-propyl bromide, is a colourless liquid of agreeable odour and bitter burning taste and decolorises bromine in the cold. The corresponding *acetate*, b. p. 162—163°/765 mm., D^{20} 0·877, obtained by the action of acetyl chloride on the alcohol, is a colourless liquid of agreeable odour. The isomeric *tert.*-alcohol, dimethylbutylcarbinol, b. p. 141—142°/755 mm., prepared by de Wael, on treatment with acetyl chloride yields the corresponding *chloride*, b. p. 130—135° (decomp.), and only decolorises bromine on warming; thus confirming Henry's suggestion (Abstr., 1907, i, 4) that bromine may be used as a differential reagent for isomeric *sec.*- and *tert.*-alcohols.

iso*Propylbutylcarbinol*, $C_4H_9{\cdot}CHPr^{\beta}{\cdot}OH$, b. p. 153—154°, D^{20} 0·825, n_D 1·42041, is a colourless liquid, less mobile than water, and has a pleasant odour and a burning taste, and is obtained, together with *iso*butyl alcohol, by the interaction of *iso*butaldehyde with magnesium butyl bromide; the corresponding *acetate*, b. p. 172°/760 mm., D^{20} 0·875, n_D 1·41664, is a colourless, mobile liquid with a pleasant odour and bitter taste. *γ-Iodo-β-methylheptane*, b. p. 160—175°, obtained by the action of red phosphorus and iodine on the alcohol, when distilled over lead hydroxide furnishes dimethylamylcarbinol, $C_5H_{11}\cdot CMe_2\cdot OH$ (Masson, Abstr., 1901, i, 250), b. p. 162°, D^{20} 0·819, n_D 1·43031, which has also been prepared by the action of ethyl *n*-hexoate on magnesium methyl iodide. On treatment with acetyl chloride, this *tert.*-alcohol furnishes the corresponding *chloride* (compare Henry, 1906, i, 781), a colourless, mobile, strongly-smelling liquid, which on heating alone, or better, with potassium hydroxide, furnishes the *octylene*, $CMe_2{:}CH\cdot C_4H_9$, b. p. 123—125°/755 mm., D^{20} 0·816, a colourless, mobile, feebly-smelling liquid, which burns with a brilliant flame and furnishes a liquid *dibromide*.

Propylisobutylcarbinol, $CH_2Pr^{\beta}\cdot CHPr^{\alpha}\cdot OH$, b. p. 160°, D^{20} 0·8207, n_D 1·42031, obtained together with amyl alcohol by the action of *iso*-valeraldehyde on magnesium propyl bromide, is a colourless, rather viscid liquid with a pleasant odour and burning taste. The corresponding *acetate*, b. p. 178°/768 mm., D^{18} 0·880, n_D 1·41554, is a colourless liquid of pleasant odour. T. A. H.

Methyl-*n*-heptylcarbinol. JOSEPH VAN GYSEGEM (*Bull. Acad. roy. Belg.*, 1906, 692—706).—*Methyl-*n*-heptylcarbinol*, $C_7H_{15}\cdot CHMe\cdot OH$, b. p. 197—198°/747 mm., m. p. −35° to −36°, D^{20} 0·84708, n_D 1·43533, prepared by the action of acetaldehyde on magnesium *n*-heptyl bromide, is a colourless, rather viscid liquid with a rancid odour and a bitter, nauseous taste. The corresponding *acetate*, b. p. 214—215°/752 mm., D^{20} 0·8804, n_D 1·42251, obtained by the action of the bromide on silver acetate in presence of ether, is a colourless liquid with a slight, fruity odour. The *chloride*, b. p. 190°/764 mm., D^{20} 0·8563, is a colourless, feebly-smelling liquid which does not solidify at −75°. The *bromide*, b. p. 140°/100 mm., and 208—209°/767 mm. (decomp.), D^{20} 1·081, n_D 1·45357, resembles the chloride, and, on treatment with potassium hydroxide or sodium methoxide or ethoxide, yields the corresponding *nonylene*, $CHMe{:}CH\cdot C_6H_{13}$, b. p. 153—154°/768 mm., D^{20} 0·8371, n_D 1·42031, which is a colourless, mobile liquid of penetrating odour and furnishes a liquid *dibromide*. The *methyl ether*, $C_7H_{15}\cdot CHMe\cdot OMe$, cannot be obtained by the action of the bromide on sodium methoxide, and was prepared by the action of the compound, $CHMeCl\cdot OMe$, on magnesium *n*-heptyl bromide. It is a mobile, pleasant-smelling liquid, b. p. 188—189°/760 mm., D^{20} 0·8228. The *ethyl ether*, b. p. 200°/757 mm., D 0·8193, n_D 1·423, similarly prepared, resembles its lower homologue.

When methyl-*n*-heptylcarbinol is oxidised with potassium dichromate and sulphuric acid, it furnishes *methyl* n-*heptyl ketone*, b. p. 191—192°/760 mm., D^{20} 0·8281, n_D 1·42791, a colourless, mobile liquid with a pleasant, fruity odour and a disagreeable taste; it furnishes a crystalline *compound* with sodium hydrogen sulphite. On oxidation with warm chromic acid mixture the ketone yields acetic and *n*-heptoic acids. Methyl *n*-heptyl ketone was prepared synthetically by the interaction of acetonitrile and magnesium *n*-heptyl bromide, but, as Blaise has observed in other cases (Abstr., 1902, i, 164), this method gives a poor yield. T. A. H.

Ethyl-*n*-hexylcarbinol. ADHÉMAR GÉRARD (*Bull. Acad. roy. Belg.*, 1906, 790—795. Compare Wagner, Abstr., 1885, 370).—This alcohol may be obtained by the action of magnesium ethyl bromide on heptaldehyde, or by the action of propaldehyde on magnesium hexyl bromide. As Konowaloff has shown, the former reaction gives rise to a mixture of the required alcohol with heptyl alcohol, from which it cannot be separated readily. By employing the second reaction, a yield equivalent to 50% of the theoretical of ethyl-*n*-hexylcarbinol, m. p. $-20°$ to $-23°$, D^{20} 0·8150, n_D 1·42791, is obtained. This is a colourless, rather viscous liquid with a disagreeable odour and a burning taste; with acetyl chloride it furnishes the corresponding *acetate*, b. p. 203—204°/761 mm., D^{20} 0·8321, a colourless, pleasant-smelling liquid. T. A. H.

Propyl-*n*-amylcarbinol. MARCEL PEXSTERS (*Bull. Acad. roy. Belg.*, 1906, 796—802).—*Propyl*-n-*amylcarbinol*, $C_5H_{11}\cdot CHPr^{\alpha}\cdot OH$, b. p. 192—193°/760 mm., D^{20} 0·8282, n_D 1·41971, prepared by the action of *n*-butaldehyde on magnesium *n*-amyl bromide, is a colourless, somewhat viscid liquid with a faintly ethereal odour and a piquant, slightly bitter taste; it does not yield a phenylurethane. The corresponding *acetate*, b. p. 199—200°/767 mm., D^{20} 0·8531, obtained by the action of acetyl chloride, is a colourless liquid with a pleasant ethereal odour.

Primary n-*amyl nitrite*, b. p. 104°/761 mm., D^{20} 0·8528, n_D 1·38506, obtained by the addition of dilute sulphuric acid to *n*-amyl alcohol dissolved in an aqueous solution of sodium nitrite, is a mobile, slightly yellow liquid with the characteristic odour of nitrous esters; it is unstable and develops an acid reaction when kept.

Primary n-*amyl mercaptan*, b. p. 126°/767 mm., D^{20} 0·8572, n_D 1·44366, prepared by the action of potassium hydrogen sulphide in alcohol on amyl bromide, is a colourless, mobile liquid with a penetrating and particularly disagreeable odour. T. A. H.

***n*-Dibutylcarbinol.** FERNAND MALENGREAU (*Bull. Acad. roy. Belg.*, 1906, 802—810).—*n*-Dibutylcarbinol, $CH(C_4H_9)_2\cdot OH$, may be obtained by the interaction of magnesium *n*-butyl bromide and either ethyl formate or *n*-valeraldehyde (compare Grignard, Abstr., 1901, i, 250). The first of these reactions furnishes *dibutylcarbinyl formate*, b. p. 194°/766 mm., D^{20} 0·870, which is a colourless, mobile, pleasant-smelling liquid. The second reaction furnishes free n-*dibutylcarbinol*, b. p. 193°/766 mm., D^{20} 0·823, and mol. refraction 44·8 (calc. 45·05). The corresponding *acetate*, b. p. 205°/770 mm., D^{20} 0·850, obtained by the action of acetyl chloride, is a mobile, pleasant-smelling liquid.

*Butyl*iso*butylcarbinol* may be prepared by the action of *iso*valeraldehyde on magnesium *n*-butyl bromide, or by the action of *n*-valeraldehyde on magnesium *iso*butyl bromide; the first of these reactions, which also give rise to some *iso*amyl alcohol, was employed in the present instance. This alcohol, $CH_2Pr^{\beta}\cdot CH(OH)\cdot C_4H_9$, b. p. 184°/766 mm., D^{20} 0·815, mol. refraction 44·83 (calc. 45·05), is a colourless, not very mobile liquid of pleasant odour. The *acetate*, b. p. 195°/768 mm.,

D^{20} 0·859, mol. refraction 55·2 (calc. 55·14), is a pleasant-smelling liquid.

The *n*-butyl alcohol, used as a starting point in the foregoing reactions, was prepared either by Grignard's method, the action of formaldehyde on magnesium propyl bromide, or by the reduction of ethyl butyrate as described by Bouveault; the former method gave a yield of 70% and the latter of 60% of the theoretical. The *n*-valeraldehyde was prepared by distilling α-hydroxycaproic acid, as suggested by Blaise, and only a 20% yield was obtained. T. A. H.

The Wax from the Palm Raphia Ruffia of Madagascar and Arachyl Alcohol. ALBIN HALLER (*Compt. rend.*, 1907, **144**, 594—598).—The wax from *Raphia Ruffia*, described by Jumelle (*Compt. rend.*, 1905, **141**, 1251), has m. p. 80°, b. p. 280—300°/10 mm. (decomp.), is completely soluble in boiling benzene, but when treated with boiling alcohol leaves 10% (m. p. 77°) undissolved. Analysis of the crude wax, the product of distillation and the portion soluble in alcohol, agree most nearly with the formula $C_{20}H_{42}O$. It is not identical with Etard's medicagol (Abstr., 1892, 746), but appears to be a saturated alcohol or mixture of alcohols. It is not attacked by boiling aqueous or alcoholic potash, and does not combine with bromine. It forms an *acetate*, $C_{20}H_{41}OAc$, with a grey colour, soft consistency, and m. p. 65°; and a *benzoate*, $C_{20}H_{41}O{\cdot}CO{\cdot}C_6H_5$, a dark brown, oily mass, m. p. 55°.

The wax when heated with zinc chloride gives a white, greasy substance which crystallises in ill-defined nacreous lamellæ, m. p. 55°. When this is distilled with phosphoric oxide, the melting point is reduced to 40°, and a repetition of the process reduces it to 36° without change in composition. The hydrocarbons so obtained combine with bromine.

The wax resists oxidation by potassium dichromate in glacial acetic acid, or by heating with potash-lime. *Arachyl alcohol*, $C_{20}H_{42}O$, a white, waxy substance, m. p. 71°, prepared by reduction of methyl arachidate, is not identical with the preceding substance. E. H.

Preparation of Ethylene Glycol and Other Alcohols. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1906, 732—740. Compare Abstr., 1897, i, 1; 1899, i, 660; 1901, i, 577; 1902, i, 736).—The author has applied the method of hydrolysis described by Haller (Abstr., 1907, i, 9), which consists in heating the requisite alkyl ester with methyl alcohol containing hydrogen chloride, to the diacetyl derivatives of ethylene and trimethylene glycols, and to pyruvyl acetate, and finds that in each of these three cases better yields of the corresponding alcohols are obtained than can be secured by the processes previously in use for their preparation. Similarly, trimethylene chlorohydrin, $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, may be prepared readily from the corresponding chloroacetate, $CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$, by this means. T. A. H.

Sodium Ethoxide. WILLIAM OECHSNER DE CONINCK and EDOUARD CHAUVENET (*Bull. Acad. roy. Belg.*, 1907, 33—34).—At a red heat, sodium ethoxide furnishes ethylene, acetylene, and hydrogen. Nitric acid yields at first ethyl nitrite and finally carbon dioxide. Other oxidising agents furnish acetaldehyde and acetic acid, but with chlorine a small quantity of monochloroacetic acid is also formed. Formic, acetic, oxalic, benzoic, and hydrochloric acids furnish the corresponding ethyl esters, but with sulphuric acid a mixture of ethyl ether and ethyl hydrogen sulphate is formed, and after prolonged action some ethylene is produced. Ethyl benzoate reacts with the ethoxide to form a number of products, among which ethyl ether and sodium benzoate were recognised. T. A. H.

The Substitution of Ethoxy-Groups by Radicles. Alexei E. Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 8—13).—A reply to Reformatsky's criticism of the author's paper on this subject (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 327, 677). Z. K.

Nitrogen Bases Formed in the Decomposition of Cephalin. H. Cousin (*J. Pharm. Chim.*, 1907, [vi], **25**, 177—180. Compare Abstr., 1906, i, 725).—Thudichum has stated that, on hydrolysis with baryta, cephalin furnishes choline and two other bases yielding platinichlorides having respectively the formulæ $(C_2H_7ON)_2,H_2PtCl_6$ and $C_5H_{14}ON_2,HCl,PtCl_4$. The author finds that on hydrolysis with hydrochloric acid the only base obtained from cephalin is choline and he suggests that the others obtained by Thudichum are probably formed by prolonged ebullition of the choline with baryta. T. A. H.

Preparation of Formates from Alkali Hydroxides and Carbon Monoxide at a High Temperature under Pressure. Elektrochemische Werke (D.R.-P. 179515).—Alkali formates are readily produced in theoretical yield when the alkali hydroxide is employed in the form of lumps as large as peas. The reaction is carried out in a closed vessel fitted with a mechanical stirrer, so that the solid materials can be continually agitated. The carbon monoxide, either pure or in the form of producer gas, is introduced under pressure, and the initial temperature is 100—120°. A small amount of moisture, about 4%, may be present, and when two-thirds of the alkali hydroxide is converted into formate, a further 2% of water is introduced. G. T. M.

Hydrogenation of Compounds Containing the Carboxyl Group by the Method of Sabatier and Senderens. Johan F. Eykman (*Chem. Weekblad*, 1907, **4**, 191—193. Compare Darzens, this vol., i, 277).—The application of the method of Sabatier and Senderens to the hydrogenation of various acids, such as undecenoic, erucic, *iso*lauronic, and others, yielded good results, indicating that the presence of the free carboxyl group does not retard the action. At about 210°, camphoric anhydride is reduced almost quantitatively to campholide, m. p. 215° (Haller gives 211°). With benzene and aluminium chloride, campholide yields phenylcampholic acid, m. p. 132°. Reduction of succinic anhydride yields γ-butyrolactone, but part of the anhydride is converted into succinic acid by the water formed. Citraconic acid undergoes partial hydrogenation into pyrotartaric acid, m. p. 112°. A. J. W.

Esterification of Castor Oil. ALBIN HALLER (*Compt. rend.*, 1907, **144**, 462—466).—When castor oil is dissolved in methyl alcohol containing 1% hydrochloric acid and heated in a reflux apparatus for several hours, there are obtained a small quantity of oenanthaldehyde, proceeding either from decomposition of the oil itself or of the methyl ricinoleate, methyl stearate, *methyl ricinoleate*, b. p. 225—227°/10 mm.; D^{15} 0·927; $[\alpha]_D$ +5°2′; n_D^{15} 1·4645, and methyl dihydroxystearate, m. p. 107—108° (Juillard, Abstr., 1895, i, 500).

Esterification of the oil with ethyl alcohol, under the same conditions, gives *ethyl ricinoleate*, b. p. 227—230°/10 mm.; D^{15} 0·918; $[\alpha]_D$ +4·48°; n_D^{15} 1·4630; whilst with *n*-propyl and *iso*butyl alcohols, n-*propyl ricinoleate*, b. p. 233—236°/10 mm.; D^{15} 0·912; $[\alpha]_D$ + 4·35°; n_D^{15} 1·4624, and iso*butyl ricinoleate*, b. p. 239—241°/10 mm.; D^{15} 0·908; $[\alpha]_D$ + 4·22°; n_D^{15} 1·4621, are obtained.

The results confirm the conclusions of previous authors of the presence in castor oil of the glycerides of stearic, ricinoleic, and dihydroxystearic acids, but do not confirm Hazura and Grüssner's discovery (Abstr., 1888, 1270) of two isomeric ricinoleins. As yet, the oxidation of methyl ricinoleate by means of potassium permanganate in acetone solution has only given a methyl trihydroxystearate, $C_{19}H_{38}O_5$, m. p. 87°, whilst the authors cited obtained two isomeric trihydroxystearic acids by oxidation of liquid ricinoleic acid.

When methyl or ethyl ricinoleate is distilled under the ordinary pressure, oenanthaldehyde and an ester of undecenoic acid are formed, $C_{18}H_{33}O_3R = C_7H_{14}O + C_{11}H_{19}O_2R$.

With methyl ricinoleate the yield of aldehyde is 62% and of methyl undecenoate 40% of the theoretical, whilst with the ethyl ester the corresponding quantities are 50% and 32% respectively.

E. H.

Action of Mercuric Acetate Dissolved in Acetic Acid on Unsaturated Fatty Acids. ALEXANDRE LEYS (*Bull. Soc. Chim.*, 1907, [iv], 1, 262—268. Compare Abstr., 1905, i, 433; ii, 655).—When oleic acid or olein is added to a solution of mercuric acetate in acetic acid and the mixture is warmed, it becomes brown and a precipitate of mercurous acetate is formed, which, unless excess of mercuric acetate is present, is further reduced to mercury. Crotonic, elaidic, and linoleic acids behave similarly, but their glyceryl and other esters do not react in this manner. The reaction appears to be confined to the monobasic unsaturated acids, but in the case of maleic acid, although no precipitate is formed, a soluble mercurous salt appears to be produced, and with succinic acid there is a formation of mercurous acetate. The other product (mercurialised olein), formed when olein is treated in this manner, can be isolated as a brown syrup, which, after a time, solidifies to a confused mass of transparent crystals and gives a yellowish-red colour with nitric acid. The mercury may be estimated in this material by dissolving it in chloroform, adding excess of iodine in alcohol, decolorising after an hour with sodium thiosulphate, separating and evaporating to dryness the aqueous layer, treating the residue with *aqua regia*, and applying Denigès's process (Abstr., 1896, ii, 385).

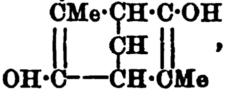
T. A. H.

Hydrogen Iodide Additive Compounds of Oleic, Elaidic, and Brassidic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 180087).—The unsaturated acids of high molecular weight on treatment with phosphorus, iodine, and water give rise to a mixture of the hydrogen iodide additive compounds and certain products containing phosphorus; the latter are removed only with great loss of the iodo-derivative. The iodation leads to pure products when it is effected with a concentrated glacial acetic acid solution of hydrogen iodide; the latter being prepared from iodine and copaiva oil.

Iodobehenic acid is obtained as a colourless solid on shaking erucic acid with rather more than the calculated amount of the hydrogen iodide solution; the operation takes several days and is effected at 60—70°.

Iodostearic acid, a pale yellow oil at the ordinary temperature, is prepared in a precisely similar manner from oleic acid, and brassidic and elaidic acids are also amenable to this process. G. T. M.

Condensation of Ethyl Acetoacetate and Formaldehyde in the Presence of Sodium Hydroxide. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1200—1204).—From the mass obtained by the action of formaldehyde on a cold solution of ethyl acetoacetate in sodium hydroxide, a *substance*, probably



$$\begin{array}{l} \mathrm{CMe\cdot CH\cdot C\cdot OH} \\ \;\| \qquad \mathrm{CH} \quad \| \\ \mathrm{OH\cdot C{-}{-}CH\cdot CMe} \end{array}$$

, has been isolated. It is amorphous and does not melt at 118°, is readily soluble in sodium hydroxide and alcohol, sparingly so in many organic solvents. It is of an acidic or phenolic character, has many of the properties of shellac, and with methyl iodide yields the *methoxy*-derivative, $C_9H_{10}(OMe)_2$. Z. K.

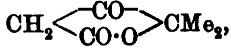
[Esters of Citrylidenealkoxyacrylic Acids.] A. MASCHMEYER (D.R.-P. 178298).—The compound obtained by condensing citral and ethyl acetoacetate has no distinctive odour of violets when warmed with strong acids, and yields a product which furnishes ionone on hydrolysis. It is now found that the condensation products, obtained from citral and the alkyl chloroacetates in the presence of the alkali ethoxides, readily yield yellow, oily substances which, although possessing an intense odour of violets, are nevertheless quite distinct from ionone.

Methyl citrylidenemethoxyacrylate, $C_9H_{15}\cdot CH{:}C(OMe)\cdot CO_2Me$, b. p. 170—200°/20 mm., is prepared by adding a cooled mixture of citral and ethyl chloroacetate to ether containing suspended sodium methoxide.

Methyl cyclo*citrylidenemethoxyacrylate*, b. p. 165—185°/21 mm., D_{25} 0·950, is produced by dissolving the foregoing ester in cold concentrated sulphuric acid and pouring the product on to ice; it may also be obtained by boiling with strong aqueous solutions of oxalic or phosphoric acid. G. T. M.

New Synthesis of Tetronic Acid. Erich Benary (*Ber.*, 1907, **40**, 1079—1083).—When ethyl sodiomalonate (2 mols.) and acetyl chloride (1 mol.) in ether are gently warmed, instead of a *cyclo*propanonedicarboxylate being produced, there is formed ethyl tetrone-4-carboxylate (Anschütz and Bertram, Abstr., 1903, i, 271), from which tetronic acid can be obtained by digestion with baryta and conversion of the barium tetronecarboxylate into tetronic acid by acidification, carbon dioxide being liberated.

After the removal of the ethyl tetronecarboxylate from the ethereal solution, there remains behind in small quantity a *compound*, $C_9H_{12}O_5$, crystallising in needles, m. p. 91—92°, the constitution of which has not yet been determined. Its aqueous solution is neutral, but it quickly changes to ethyl tetronecarboxylate, and this compound is likewise obtained on treatment with bromine. With phenylhydrazine it yields a *phenylhydrazide*, $C_{18}H_{14}O_4N_2$, a white powder, m. p. 188—189° (decomp.), giving Bülow's reaction. Dry ammonia gas gives a *compound*, $C_7H_9O_4N$, a white powder, m. p. 243° (decomp.). Hydroxylamine gives a monobasic *hydroxamic acid*, $C_7H_9O_5N$, m. p. 180° (decomp.), which gives an intense bluish-violet coloration with ferric chloride.

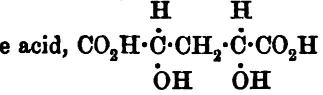
The interaction of bromo*iso*butyl bromide and ethyl malonate results in the formation of 3 : 3-*dimethyltetronic acid*,  $CH_2{<}\genfrac{}{}{0pt}{}{-CO-}{CO\cdot O}{>}CMe_2$, crystallising from benzene in colourless leaflets, m. p. 142—143°. The aqueous solution with ferric chloride and sodium nitrite gives the same characteristic colorations as tetronic acid. W. R.

Mutual Interconversion of Optically Active Bromosuccinic and Aspartic Acids. Emil Fischer and Karl Raske (*Ber.*, 1907, **40**, 1051—1057. Compare this vol., i, 192).—Although Tilden and Marshall (Trans., 1895, **67**, 494) converted aspartic into optically active chlorosuccinic acid by means of nitrosyl chloride, the opposite change has not yet been effected; the product described by Walden and Lutz (Abstr., 1898, i, 127), produced by the interaction of methyl-alcoholic ammonia and *l*-bromosuccinic acid, being possibly a monoamide of malic acid.

l-Bromosuccinic acid when treated with aqueous ammonia cooled at first to − 40° and subsequently maintained for a day at + 3° was converted into an amorphous mass from which *d*-aspartic acid, $[\alpha]_D^{20}$ − 25·47°, was isolated. A Walden re-arrangement takes place (compare Walden, Abstr., 1896, i, 205; 1898, i, 127, 178; 1899, ii, 538; Fischer, this vol., i, 192), and, similarly, from ethyl *l*-aspartate and nitrosyl bromide, ethyl *d*-bromosuccinate was obtained. The replacement of the amino-group by halogen takes place in two stages, perbromides being first formed.

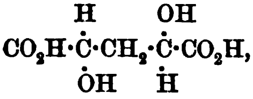
The *dibromide* of *ethyl* l-*aspartate hydrobromide* is obtained as an oil solidifying in the cold to a mass of reddish-yellow crystals which decompose when warmed, but can be kept at 0° in a vacuum for some little time. The *dibromide* of l-*aspartic acid hydrobromide* forms glistening, brown needles or prisms which decompose slowly even below 0°. E. F. A.

$\alpha\gamma$-Dihydroxyglutaric Acids. HEINRICH KILIANI and O. MATTHES (*Ber.*, 1907, 40, 1238—1242. Compare Kiliani and Herold, Abstr., 1905, i, 739).—It has been overlooked previously that loss of carbon dioxide from *iso*saccharic acid must lead to the formation of a mixture of two $\alpha\gamma$-dihydroxyglutaric acids, consisting of the optically inactive acid,



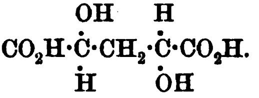
$CO_2H\cdot\overset{H}{\underset{OH}{C}}\cdot CH_2\cdot\overset{H}{\underset{OH}{C}}\cdot CO_2H$

and one of the two active acids,



$CO_2H\cdot\overset{H}{\underset{OH}{C}}\cdot CH_2\cdot\overset{OH}{\underset{H}{C}}\cdot CO_2H$,

and



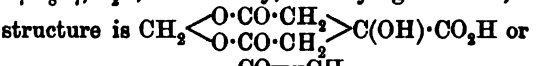
$CO_2H\cdot\overset{OH}{\underset{H}{C}}\cdot CH_2\cdot\overset{H}{\underset{OH}{C}}\cdot CO_2H$.

This is now shown experimentally to be the case; the configuration of the active acid remains to be established. The acids are separated by means of the calcium salts, that of the active acid being much the more soluble.

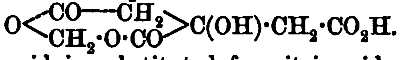
The lactone of the *i*-acid, $C_5H_6O_4$, m. p. 167—168°, is anhydrous; the calcium, zinc, and copper salts have the properties described previously (*loc. cit.*); the *silver*, *brucine hydrogen*, $(C_{23}H_{26}O_4N_2,C_5H_8O_6)_2,H_2O$, m. p. 238° (decomp.), $[\alpha]_D$ $-29 \cdot 3°$, and *brucine*, $(C_{23}H_{26}O_4N_2)_2,C_5H_8O_6$, m. p. 222—223°, salts are described.

d-*$\alpha\gamma$-Dihydroxyglutaric acid*, $C_5H_8O_6$, crystallises in prisms, m. p. 125°, $[\alpha]_D$ $+ 3 \cdot 9°$, and does not form a lactone. The *calcium*, *zinc* $(+2/7H_2O)$, *copper*, *silver*, *quinine*, m. p. 156°, *brucine hydrogen*, m. p. 151°, $[\alpha]_D$ $-24 \cdot 4°$, and *brucine* $(+7H_2O)$, m. p. 128—129°, or when anhydrous, 203°, salts are described. G. Y.

Condensation of Some Hydroxy-Acids and Formaldehyde in the Presence of Picric Acid. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1211—1216).—By the action of formaldehyde on citric acid in the presence of picric acid, a *substance*, $C_7H_8O_7 + 2H_2O$, m. p. 98—118°, was isolated; when melted, it loses water, forming first $C_7H_8O_7,H_2O$, and finally, on drying at 118°, $C_7H_8O_7$. Its probable structure is



or



When tartaric acid is substituted for citric acid, a *substance*, probably $2C_6H_2(NO_2)_3\cdot OH,C_6H_6O_6$, m. p. 115—117°, is formed. It is soluble in water and most organic solvents, but in water and in alcohol it decomposes with liberation of picric acid. The form and colour of the crystals obtained depend on the relative proportions of the reacting substances. As might be expected from the formula, the substance is explosive. Z. K.

Carbithionic Acids. II. Dithioacetic Acid. JOSEF HOUBEN and HEINRICH POHL (*Ber.*, 1907, 40, 1303—1307. Compare Abstr., 1906, i, 847).—Whilst the thioacyl disulphides are stable compounds, the carbithionic acids have been characterised only in the form of salts or derivatives. It has been found possible now to isolate carbithionic acids of the aliphatic series in a state of purity and, of these, methylcarbithionic acid is described in the present paper.

Methylcarbithionic acid [*dithioacetic acid*], $CH_3\cdot CS\cdot SH$, prepared by the action of carbon disulphide on magnesium methyl iodide in cooled absolute ethereal solution and decomposition of the product with ice and cooled hydrochloric acid, is obtained as a reddish-yellow oil, b. p. 37°/15 mm., D^{20} 1·24, is readily soluble in organic solvents, and displaces acetic and formic acids from their salts. It is readily oxidised, forms thioacetyl disulphide when shaken with water, but inflames only when heated, colours paper reddish-yellow, and produces black spots on the skin. The *alkali*, *alkaline earth*, *aluminium*, and *magnesium* salts are soluble in water; the neutral solutions give coloured precipitates with salts of the heavy metals. The dithio-acid yields a viscid, yellow mass when saturated with hydrogen chloride, forms thioacetyl disulphide when treated with iodine in potassium iodide solution, and is reduced in alkaline solution to a yellow, odourless *oil*. G. Y.

Ester-Acids of Sulphur-substituted Carbonic Acids with Aliphatic Hydroxy-Acids. II. B. HOLMBERG (*J. pr. Chem.*, 1907, [ii], 75, 169—187. Compare Abstr., 1905, i, 323).—One trithio-, three dithio-, and three monothio-carboglycollic acids may be derived from carboglycollic acid, $OH\cdot CO\cdot O\cdot CH_2\cdot CO_2H$, by substitution of sulphur for oxygen atoms. These acids are unstable in the free state. In the present paper, derivatives of the trithio- and of one of the dithio-acids are described. Such ester-acids may be formed by addition of carbon disulphide to glycollic or thioglycollic acid in alkaline solution; by double decomposition of the resulting monoglycollic acids with alkyl haloids or salts or esters of halogen-substituted acids; by oxidation of the higher sulphur acids, the sulphur atoms being substituted partially by oxygen; by the action of carbonyl or thiocarbonyl chloride on hydroxy- or mercapto-acids, and by decomposition of other related compounds.

In the nomenclature of the sulphur derivatives of carboglycollic acid, the author now uses the term "Δ-thio-" in place of "sulpho-" previously employed to denote a sulphur atom doubly linked to carbon, and distinguishes the other two sulphur atoms of the trithiocarbonic group, when necessary, as α- and β-thio-, thus

$$SEt\cdot CS\cdot O\cdot CH_2\cdot CO_2H$$

becomes ethyl αΔ-dithiocarboglycollic acid, $OEt\cdot CS\cdot S\cdot CH_2\cdot CO_2H$ is ethyl βΔ-dithiocarboglycollic acid, whilst $SEt\cdot CO\cdot S\cdot CH_2\cdot CO_2H$ is ethyl dithiocarboglycollic acid.

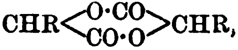
Dithiocarbodiglycollic acid has the conductivity constant $K = 0{\cdot}156$ with $\infty = 378$; trithiocarbodiglycollic acid, with $\infty = 378$, has $K = 0{\cdot}26$.

Potassium αΔ-dithiocarboglycollate, $SK\cdot CS\cdot O\cdot CH_2\cdot CO_2K$, formed by the action of carbon disulphide on glycollic acid in aqueous potassium hydroxide solution, separates on addition of alcohol as a yellow, crystalline crust. The *lead* salt was analysed. With potassium chloroacetate, the potassium salt yields αΔ-dithiocarbodiglycollic acid (*loc. cit.*). On liberation, the monoglycollic acid forms a yellow oil which decomposes immediately into glycollic acid and carbon disulphide. *Ethyl αΔ-dithio-*

carboglycollic acid, formed by the action of ethyl bromide on the potassium salt in aqueous solution, crystallises in slightly yellow needles, m. p. 77—78°, and, with $\infty = 378$, has the conductivity constant $K = 0{\cdot}212$; the *potassium* $(+H_2O)$, *sodium* $(+3H_2O)$, and *barium* $(+2H_2O)$ salts are described. The ethyl-acid is decomposed by alcoholic potassium hydroxide at the ordinary temperature, yielding ethyl mercaptan, potassium glycollate, and potassium ethyl thiocarbonate. When heated in neutral solution, the potassium salt of the ethyl-acid decomposes, forming carbon dioxide, hydrogen sulphide, ethyl mercaptan, and potassium glycollate. The action of aqueous ammonia on the ethyl-acid leads to the formation of ethyl mercaptan and *ammonium thiocarbamylglycollate,* $NH_2{\cdot}CS{\cdot}O{\cdot}CH_2{\cdot}CO_2NH_4$, which separates, on evaporation of the aqueous solution, as a white, crystalline mass. The *acid* crystallises from alcohol in colourless plates, m. p. 111—112°, and can be titrated with *N*-sodium hydroxide and phenolphthalein.

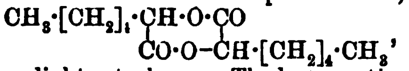
Potassium trithiocarboglycollate, $SK{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2K$, formed by the action of carbon disulphide and potassium hydroxide on thioglycollic acid in aqueous solution, crystallises in yellowish-red needles or leaflets, gives coloured *precipitates* with salts of the heavy metals, and with potassium chloroacetate forms potassium trithiocarbodiglycollate.

The action of a chloroacetate on potassium ethyl trithiocarbonate, in aqueous solution cooled by ice, leads to the formation of ethyl trithiocarbonate, trithiocarbodiglycollic acid, and *ethyl trithiocarboglycollic acid,* $SEt{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, which is formed also in small amount by the action of ethyl bromide on potassium trithiocarboglycollate. It crystallises in yellow needles or thin prisms, m. p. 75·5—76°, is soluble in chloroform, with $\infty = 378$ in aqueous solution, has the conductivity constant $K = 0{\cdot}082$, and decomposes slowly at the ordinary temperature. The *calcium* salt crystallises in two forms, differing in their water of crystallisation; the more stable $(+3H_2O)$ was analysed. The *amide,* formed from chloroacetamide and potassium ethyl trithiocarbonate, crystallises in thin, golden leaflets, m. p. 123·5—124°. Ethyl trithiocarboglycollic acid is decomposed only slightly by water; in neutral solution it yields ethyl trithiocarbonate and potassium trithiocarbodiglycollate slowly at the ordinary temperature, quickly at 50—60°, whilst at higher temperatures decomposition of the trithiocarbodiglycollic acid takes place. The partial decomposition takes place rapidly in aqueous alkaline solution at the ordinary temperature, whilst the products of complete decomposition are obtained by the action of alcoholic potassium hydroxide or ammonia. Aqueous ammonia acts partly as an alkali, but forms also a *product* which is probably thiocarbamylthioglycollic acid. The oxidation of ethyl trithiocarboglycollic acid by dilute potassium permanganate does not stop at ethyl dithiocarboglycollic acid, but proceeds to the formation of products such as ethylsulphonic and thioacetic acids. G. Y.

Preparation of Acyclic Aldehydes. I. P. BAGARD (*Bull. Soc. chim.*, 1907, [iv], 1, 307—320. Compare Blaise, Abstr., 1904, i, 369; Le Sueur, Trans., 1904, 85, 827, 1708).—When an α-hydroxycarboxylic acid is heated, it loses water and gives rise to the production of a small quantity of the corresponding dilactide,  $CHR{<}\genfrac{}{}{0pt}{}{O\cdot CO}{CO\cdot O}{>}CHR$, and a considerable amount of non-volatile acid product, probably constituted of hemipolylactides of the type

$$CO_2H\cdot CHR\cdot O\cdot CO\cdot CHR \ldots . O\cdot CO\cdot CHR\cdot OH.$$

Both these products on further heating furnish an aldehyde containing one carbon atom less than the acid initially employed, and in addition small quantities of unsaturated acids and olefinic hydrocarbons, these two by-products being formed by loss of water and carbon dioxide from the hydroxy-acid or the dilactide. The esters of the α-hydroxy-acids distil unchanged, but the corresponding alkyloxy-acids and acyloxy-acids when heated decompose, furnishing the corresponding lower aldehydes without any intermediate change, and give a better yield of the aldehydes than is obtained from the parent hydroxy-acids. The α-hydroxy-acids employed in this investigation have been prepared by the series of reactions already described by Blaise (*loc. cit.*).

Ethyl-α-hydroxyheptoate has b. p. 106°/14·5 mm. The *anilide* of the acid, m. p. 70°, crystallises from a mixture of ethyl acetate and light petroleum. The *toluidide*, m. p. 103°, crystallises from ethyl acetate. When α-hydroxyheptoic acid is heated, it furnishes, in addition to hexaldehyde (Lieben and Janecek, Abstr., 1877, 879) and butylethylene (Schorlemmer, Abstr., 1880, 158), (*a*) *γ-heptolactone*, b. p. 118—120°/15 mm., which by Blaise and Luttringer's method (Abstr., 1905, i, 329) yields *hydrazino-γ-heptolactone*, m. p. 88—89°, crystallising from ethyl acetate in flattened needles; (*b*) an unsaturated acid, b. p. 123—124°/20 mm., which was not obtained pure, and did not give concordant combustion results for heptenoic acid, and (*c*) *α-hydroxyheptolactide*,  $\begin{array}{l} CH_3\cdot[CH_2]_4\cdot CH\cdot O\cdot CO \\ \qquad\qquad\quad\ \ CO\cdot O-CH\cdot[CH_2]_4\cdot CH_3 \end{array}$, m. p. 88°, which crystallises from light petroleum. The last-mentioned substance, which can only be isolated when the reaction is stopped at an early stage, when heated to 280—300° yields carbon monoxide and hexaldehyde, and leaves an amorphous, viscous residue of acid reaction, which is probably a hemipolylactide.

When *α-acetoxyheptoic acid*, obtained as an oily product by the action of acetyl chloride on the hydroxy-acid, is heated, it yields carbon monoxide, acetic acid, and hexaldehyde, the yield of the last being 68·7%, that is, 18% higher than is obtained by distilling the hydroxy-acid itself.

Hexaldehydesemicarbazone, m. p. 106°, crystallises from a mixture of benzene and light petroleum. The *oxime*, m. p. 51°, separates in long crystals from methyl alcohol. The *azine*, $(CH_3\cdot[CH_2]_4\cdot CH{:}N)_2$, b. p. 132°/13 mm., is a colourless liquid which is very unstable. 2-n-*Amylnaphthacinchonic acid*, m. p. 255—260°, obtained by the action of pyruvic acid and β-naphthylamine on the aldehyde, is a crystalline powder, and separates from formic acid on the addition of methyl alcohol. The *diethylacetal* of the aldehyde, b. p. 90°/30 mm., is a colourless liquid.

T. A. H.

Molecular Compounds of Magnesium Bromide and Iodide with Aldehydes, Ketones, and Acetals. Boris N. Menschutkin (*Zeitsch. anorg. Chem.*, 1907, **53**, 26—33. Compare Abstr., 1904, i, 215; 1906, i, 131, 132, 552).—The molecular compounds described in the paper were obtained by direct action of the organic compounds on the dietherates of the magnesium halides.

The *compound*, $MgBr_2,3C_6H_5\cdot CHO$, occurs in small, hygroscopic plates, m. p. 159°; $MgI_2,6C_6H_5\cdot CHO$ melts at 139°. The solubility curve of these compounds in benzaldehyde has been determined from 0° to their respective melting points. The compound $MgBr_2,3CH_3\cdot CHO$ has also been obtained; it undergoes partial decomposition on fusion.

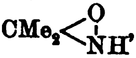
Compounds of the respective formulæ $MgBr_2,3COMe_2$ (m. p. 92°) and $MgI_2,6COMe_2$ (m. p. 106·5°) have also been prepared and the solubility in acetone from 0° to the respective melting points determined.

At low temperatures, magnesium bromide forms a compound with chloral hydrate, probably $MgBr_2,3CCl_3\cdot CH(OH)_2$, but at higher temperatures, owing to partial dissociation of chloral hydrate, magnesium bromide hexahydrate is also produced.

With methylal, the *compound* $MgBr_2,2CH_2(OMe)_2$, m. p. 112°, was obtained. Acetal gives with the iodide a *compound*,

$$MgI_2,2CH_3\cdot CH(OEt)_2,$$

m. p. 86°. The mutual solubility of these compounds and methylal and acetal respectively is very small. G. S.

Methylation of Oximino-compounds. Giacomo Ponzio and G. Charrier (*Rend. Accad. Sci. Torino*, 1907, **42**, 328—336).—The ordinary method of preparing methyl derivatives of oximino-compounds by the action of methyl iodide in presence of sodium methoxide is somewhat tedious, and in the case of the aliphatic ketoximes gives very small yields, acetoxime, for example, acting in the two tautomeric forms, $CMe_2{:}N\cdot OH$ and  $CMe_2<\overset{O}{\underset{NH}{|}}$, and giving rise to both the *O*-methyl ether and the *N*-methyl ether (compare Dunstan and Goulding, Trans., 1901, **79**, 628).

The following method for preparing the *O*-methyl ethers of oximino-compounds is simple, and can be applied to compounds of the aromatic series. The oximino-derivative (1 mol.), dissolved in an excess (4 mols.) of 30% sodium hydroxide solution, is agitated with commercial methyl sulphate (1·5 mols.). This reaction, which should be moderated by cooling the mixture, gives a yield of 60—90% of the *O*-methyl ether; the latter, being insoluble in the alkaline liquid, can generally be isolated directly.

Methylethylketoxime O-*methyl ether*, $CMeEt{:}N\cdot OMe$, is a pleasant-smelling liquid, b. p. 95°/739·3 mm.; the *platinichloride*,

$$C_5H_{11}ON,H_2PtCl_6,$$

forms yellow prisms. When the ether is boiled with 10% hydrochloric acid solution in a reflux apparatus it undergoes hydrolysis, yielding methyl ethyl ketone. The semicarbazone of the latter separates immediately if the ketone is shaken with an acetic acid solution of semicarbazide (compare Scholtz, Abstr., 1896, i, 343), and crystallises from a mixture of benzene and light petroleum in white prisms, m. p. 143—144°; Scholtz (*loc. cit.*) gave m. p. 135—136°. On evaporating on a water-bath a hydrochloric acid solution of the ether, the latter partly resinifies and is partly converted into ammonium chloride.

Benzophenoneoxime *O*-methyl ether crystallises from light petroleum in white laminæ, m. p. 102°; Spiegler (Abstr., 1884, 1155) gave m. p. 92°.

The *O*-methyl ethers of acetoxime, benzaldoxime, anisaldoxime, camphoroxime, and *iso*nitrosocamphor were also prepared. T. H. P.

Application of Metallic Calcium to Reductions in the Sugar Series. CARL NEUBERG and FRITZ MARX (*Zeitsch. Ver. deut. Zucker-ind.*, 1907, **615**, 456—461).—The use of sodium amalgam for effecting the reduction of the sugars or their derivatives, such as that of lactones to aldoses, or that of aldoses or ketoses to the corresponding alcohols, involves the subsequent difficulty of separating sodium salts from the carbohydrate derivative. This difficulty is avoided by replacing the sodium amalgam by calcium, which has the further advantage that it can be used either directly, best in the form of coarse turnings, or as calcium amalgam. The authors illustrate the mode of using calcium or its amalgam as a reducing agent by examples, and describe a crystalline alcohol, lactobiotitol, obtained by the reduction of lactose; this compound is the first alcoholic derivative of a disaccharide to be prepared in a crystalline condition.

The preparation of calcium amalgam by the method of Moissan and Chavanne (*Compt. rend.*, 1905, **140**, 122—127; Abstr., 1905, ii, 163) is troublesome, as the development of heat during the shaking of the mercury and calcium usually results in the breaking of the flask. Large quantities of the amalgam can be prepared in a single operation as follows. A spacious, thick, porcelain mortar, after being slowly heated to 100° in an oven, is charged with the required amount of mercury, and then with a little of the calcium in the form of grits (Calciumgries), the two metals being then rubbed together with a warm pestle. The formation of amalgam soon begins and, after the remainder of the calcium has been added, is continued at a rapid rate by the heat developed. In the authors' experiments a 3% calcium amalgam was employed.

The reductions of dextrose to *d*-sorbitol, of *d*-galactose to dulcitol, and of dextroseoxime to *d*-glucamine are readily effected by gradually adding calcium turnings to a 2·5% solution of the compound, which is kept cooled and well shaken whilst a current of carbon dioxide is passed through it.

Lactobiotitol, $C_{12}H_{24}O_{11}$, obtained in small yield by the gradual addition of a large excess of calcium amalgam to an aqueous lactose solution through which a current of carbon dioxide is kept passing, forms colourless crystals, begins to turn brown at about 200° and is not melted even at 280°, although at this temperature small quantities of a white sublimate are formed. It dissolves readily in water and sparingly in alcohol and, when boiled with acid, is apparently hydrolysed to galactose and sorbitol: $C_{12}H_{24}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{14}O_6$. T. H. P.

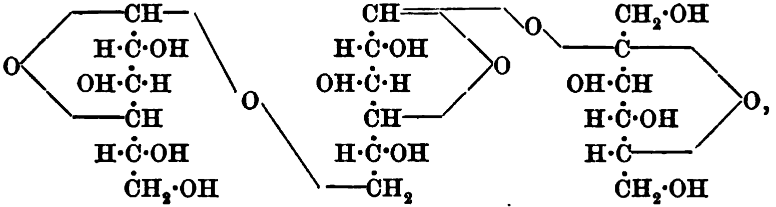
Viscosity of Solutions of Sucrose and Invert Sugar. HENRY PELLET and CH. FRIBOURG (*Chem. Zentr.*, 1907, i, 631; from *Bull. Assoc. Chim. Sucr. Dist.*, **24**, 666—668. Compare this vol., i, 185).—Experiments have been made with solutions of sucrose and invert sugar which have the same concentration, 65° Brix. The solutions contain the following proportions of sucrose and invert sugar respectively, 100 + 0, 88 + 12, 82 + 18, 77 + 23, 71 + 29, 64·5 + 35·5, 57 + 43, 49 + 51, 41 + 59, and 0 + 100. The number of seconds required for the flow of 50 cm. are respectively 225, —, 195, 180, 172, 166, 155, —, 146, and 115, and the relative viscosities 1, —, 0·87, 0·80, 0·76, 0·74, 0·69, —, and 0·65. The viscosity of solutions of sucrose and invert sugar is nearly twice as great at 27° as at 40°. E. W. W.

Kjeldahl's Method: Rapidity of Oxidation of Sucrose by Means of Sulphuric Acid. JAROSLAV MILBAUER (*Zeitsch. Zucker-ind. Böhm.*, 1907, **31**, 350—353. Compare Bredig and Brown, Abstr., 1904, ii, 247).—The author has measured the velocity of oxidation of sucrose (0·05 gram) by 94·9% sulphuric acid (50 c.c.) at 213°. A constant current of carbon dioxide was passed through the heated mixture of sugar and acid to expel the sulphur dioxide, which was absorbed and determined iodometrically. During twelve hours the rate of evolution of sulphur dioxide was practically constant, namely, 0·13 mg. per minute. The effects of a number of catalysts on the reaction were determined, the only ones found to increase the velocity appreciably being copper sulphate (1·9614 gram of the crystallised salt) and mercuric sulphate (added in the form of 0·5399 gram of mercuric oxide), the evolution of sulphur dioxide being at the rates of 0·19 and 0·37 mg. per minute in the two cases; with cobalt sulphate (0·6406 gram CoO), the rate was 0·16 mg. per minute. T. H. P.

Formation of Formaldehyde in the Combustion of Sugar. AUGUSTE TRILLAT (*Chem. Zentr.*, 1907, i, 630; from *Bull. Assoc. Chim. Sucr. Dist.*, **24**, 611—612. Compare Abstr., 1906, i, 401, 476).—In reference to a paper by Herzfeld (*Jahresber. Inst. Zuckerind.*) in which doubt is expressed as to the formation of formaldehyde by the combustion of sugar, the author points out that the blue coloration with magenta paper is also produced by acetaldehyde and propaldehyde. In his opinion the dimethylaniline test is the best; the quantity of tetramethyldiaminodiphenylmethane may be determined gravimetrically. E. W. W.

Resolution of Raffinose into Sucrose and Galactose. CARL NEUBERG (*Zeitsch. Ver. deut. Zuckerind.*, 1907, **615**, 440—453).—Up to the present all the various means adopted for the resolution of raffinose into simpler sugars have given rise, in the first place, to lævulose and melibiose, and, finally, to lævulose, dextrose, and galactose. The author finds that emulsin is capable of hydrolysing raffinose, the resultant sugars being, however, galactose and sucrose.

This result affords conclusive proof of the existence of a sucrose complex in the raffinose molecule, thus confirming the suspicion based on the observation that raffinose is hydrolysed by invertase. Since emulsin, according to Fischer, only attacks compounds having β-glucoside structures, raffinose must be looked on either as the β-galactoside of sucrose or as the lævuloside of melibiose. The formula of raffinose is hence:



which is uncertain only as regards the constitutions of the sucrose and melibiose, that is, as regards the mode of the anhydride formation between the hydroxyl groups of the separate monosaccharides.

By the conversion of raffinose into galactose and sucrose, the latter makes its first appearance as a product of the resolution of a more complex, naturally occurring sugar. This change may, indeed, be of interest to vegetable physiology. The principal source of raffinose, the sugar-beet, contains this sugar in amounts varying from mere traces to quantities such that the molasses contains as much as 22% of raffinose. The content of raffinose is often increased abnormally by disturbance of the growth, such as is caused, for example, by the sudden occurrence of frost. It must be assumed that, under these conditions, greatly increased amounts of galactans and pectic substances containing galactose residues undergo hydrolysis, the galactose liberated combining, as the result of abnormal fermentative processes, with sucrose to form raffinose. The action of emulsin on raffinose may find industrial application in the treatment of beet-sugar products containing notable proportions of raffinose. The action also affords a means of detecting small quantities of raffinose (compare Neuberg and Marx, this vol., ii, 408).

The rare sugar stachyose, which is a non-reducing tetrasaccharide of the formula $C_{24}H_{42}O_{21}$ and yields, on complete hydrolysis, 2 mols. of galactose, 1 mol. of lævulose, and 1 mol. of dextrose, is also decomposed by emulsin, but, owing to paucity of materials, the products have not yet been characterised. T. H. P.

Acetyl Derivatives of Cellobiose. Emil R. von Hardt-Stremayr (*Monatsh.*, 1907, 28, 63—72).—It is found that Skraup and Geinsperger's octa-acetylcellobiose (Abstr., 1906, i, 67), m. p. 198°, $[\alpha]_D$ + 30·51°, is identical with Maquenne and Goodwin's second octa-acetylcellobiose (Abstr., 1904, i, 799), the transformation of which into Skraup and König's compound, m. p. 228° (Abstr., 1902, i, 135), is confirmed. Attempts to bring about the reverse transformation were unsuccessful. G. Y.

Reducing Properties of Various Celluloses. Carl G. Schwalbe (*Ber.*, 1907, **40**, 1347—1351).—The author has studied the reducing properties of various celluloses. The percentage of water in the sample is first determined. In a second air-dried specimen the reducing property is then estimated and the result calculated for dry cellulose. The cupric reducing power of cellulose is estimated by mixing 3 grams of the air-dried, finely-divided specimen with 200 c.c. of water and boiling for quarter of an hour with 100 c.c. of Fehling's solution. The amount of copper in the precipitated cuprous oxide is estimated electrolytically, using a rotating electrode.

Pure celluloses exhibit very little reducing property (from 1·1 to 1·8). Hydrocellulose and oxycellulose, on the other hand, had the numbers 5·2 and 7·9 respectively. A specimen of "over-bleached cellulose" gave a value so high as 19·3. A. McK.

Theory of the Nitration of Cellulose. A. V. Saposhnikoff (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1192—1200. Compare Abstr., 1905, ii, 583).—When sulphuric acid is added to any solution of nitric acid in water, the vapour pressure of the solution increases until the system $HNO_3 + n(H_2SO_4,H_2O)$ is reached, when it is a maximum and is equal to the vapour pressure of pure nitric acid mixed with pure sulphuric in this proportion. Concurrently with this change in the vapour pressure, not only does nitric acid of sp. gr. less than that required for the nitration of cellulose acquire the power to react, but the nature of the nitration products formed also vary considerably. Tables and curves are given showing this relation. Sulphuric acid thus has the power of abstracting the water from the nitric acid without itself interfering with the process of nitration, even when it is present in considerably larger quantity than that necessary for fixing all the water, providing only that it does not decompose the nitric acid with formation of higher oxides of nitrogen. The highest nitration product obtained contained 13·4% of nitrogen, and to obtain cellulose nitrates still richer in nitrogen it will be necessary most probably to work with mixtures $HNO_3 + n(H_2SO_4,H_2O)$, where *n* has a high value. The lowest nitration product is obtained when the ratio of water to nitric acid is HNO_3,H_2O or H_3NO_4, the vapour pressure of this mixture, or possibly compound, is only 2 mm.

What must be the nature of the nitric acid which gives rise to nitration products between the higher and lower limit has not yet been elucidated. Z. K.

Decomposition of Cellulose Nitrate at Temperatures Below that of Ignition. A. V. Saposhnikoff (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1186—1192. Compare Abstr., 1906, i, 68).—The experiments on cellulose nitrate of the formula $C_{24}H_{31}(NO_3)_9O_{11}$ were performed in a similar manner to those described previously. The temperatures of decomposition can be divided into three zones. Between 160° and 150° all the nitrogen and most of the hydrogen is lost; between 145° and 130° less of both these elements are lost; at 125° and below, very little nitrogen is liberated, but the water formed is still high. Above 160° the substance explodes after thirty to forty minutes' heating. The substances liberated are carbon dioxide, nitric oxide, carbon monoxide, nitrogen, and water. The appearance of the residue varies considerably with the temperature to which the cellulose nitrate has been subjected. A curve is drawn showing the rate of decomposition at various temperatures, from which it is deduced that the rate of decomposition decreases with the fall in temperature. For the intervals 125—140°, $(dv/dt)_{max} = -24\cdot6 + 0\cdot201t$, and for 145—155°, $(dv/dt)_{max} = -136\cdot5 + 0\cdot985t$. Z. K.

Acetylation of Some Oxycelluloses. EMIL R. VON HARDT-STREMAYR (*Monatsh.*, 1907, **28**, 73—78).—Skraup and König's octa-acetylcellobiose, m. p. 228° (Abstr., 1902, i, 135), is obtained, in almost the same amount as from cellulose, on acetylation by Maquenne and Goodwin's method (Abstr., 1904, i, 799) of hydralcellulose (Bumcke and Wolffenstein, Abstr., 1899, i, 852), or of oxycellulose formed by the action of potassium chlorate and hydrochloric acid on cotton wool (Tollens, Abstr., 1901, i, 453), or of nitric acid on sawdust (Faber and Tollens, Abstr., 1899, i, 854). Only about one-third of the same amount of the octa-acetyl compound is obtained from "acid-cellulose" (Bumcke and Wolffenstein, *loc. cit.*). G. Y.

Colloidal Properties of Starch. EUGÈNE FOUARD (*Compt. rend.*, 1907, **144**, 501—503).—Fernbach and Wolff's soluble starch was treated five times with acid and washed with water until the electric conductivity of the water remained constant. It was found that the total ash diminished slightly with each treatment, falling from 0·331% to 0·124%, whilst the phosphoric acid was reduced from 0·1915% to 0·1117%. The phosphorus is not present in organic combination as might be supposed from its persistence in remaining. Whilst the acidity of 5% solutions of the five successive preparations using phenolphthalein was found to diminish from 0·212% to 0·172% the results with methyl-orange were 0·162% to 0·010%. The pseudo-solutions which are not absolutely transparent lose a considerable proportion of their acidity when filtered, although coincidently only some milligrams of starch are held back. The undissolved starch grains, therefore, fix the acid withdrawn from the colloidal medium, and the coagulation of the colloidal starch is correlative to fixation of acid. Addition of acid accelerated coagulation especially at low temperatures, whilst heat or alkalis reproduce the pseudo-soluble state. Colloidal starch is the first well-defined organic colloid which exhibits the phenomena of reversibility. N. H. J. M.

Separation of Ammonia and Methylamine. MAURICE FRANÇOIS (*Compt. rend.*, 1907, **144**, 567—569).—When a current of air charged with a mixture of ammonia and methylamine and dried is passed over yellow mercuric oxide the ammonia is absorbed to form ammonio-mercuric oxide, and the methylamine so purified may be collected in water or hydrochloric acid. The elimination of the ammonia may be more rapidly accomplished by agitating an aqueous solution containing the mixture of ammonia and methylamine with yellow mercuric oxide during one hour. The decanted liquid yields on distillation a solution of methylamine free from ammonia. The latter may also be separated from dimethylamine, trimethylamine, ethylamine, diethylamine, or triethylamine by these methods, although the dry process is difficult of application in the cases of di- and triethylamine. T. A. H.

Tetramethylammonium Platinocyanide. Jaroslav Milbauer (*Zeitsch. anorg. Chem.*, 1907, 53, 135—136).—This compound, $Pt(NMe_4)_2(CN)_4$, prepared by neutralising tetramethylammonium hydroxide with hydrogen platinocyanide, $H_2Pt(CN)_4$, occurs in colourless crystals which are readily soluble in water and completely decomposed on heating; they are not dichroic, and show no triboluminescence. The results of crystallographic measurements are also quoted. G. S.

Influence of Cyclic Linkings on the Degree of Stability of Complex Compounds. Leo Tschugaeff (*J. pr. Chem.*, 1907, [ii], 75, 153—168. Compare Abstr., 1904, i, 478; 1905, i, 743, 865; 1906, i, 814, 984).—The analogy of complex compounds (metal-alkylammines, -imides, -oximes, -glyoximes, &c.) with carbon compounds is apparent from the expositions of Werner and of Pfeiffer (Abstr., 1905, i, 33). The known cyclic complex compounds are discussed with the object of investigating the influence of cyclic linkings on the degree of stability of such substances. It is concluded that in general and especially in the case of compounds of the metals of group VIII of the periodic system, cyclic complex compounds are more stable than the corresponding acyclic compounds, and that, *ceteris paribus*, there is a marked tendency to the formation of penta-atomic rings. Stable hexa-atomic cyclic complex compounds are also formed, but there appears to be little or no tendency to the formation of tetra-, hepta-, or octa-atomic ring systems. G. Y.

Hexamethylenetetramine and its Salts (Cystopurine). Peter Bergell (*Chem. Zentr.*, 1907, i, 487—488; from *Deut. med. Woch.*, 33, 55—56).—A method of preparing hexamethylenetetramine in the form of the hydrochloride by evaporating urine to which ammonia has been added, mixing the residue with dry sodium sulphate, drying, treating with chloroform, extracting the residue with alcohol, and finally precipitating by means of hydrogen chloride is described. In order to estimate the quantity, the sample of urine is acidified with acetic acid, mercuric chloride added, the solution filtered after remaining twenty-four hours, and the precipitate after washing with a solution of mercuric chloride containing acetic acid, treated by Kjeldahl's method. When 50 c.c. of urine are used, the nitrogen is determined in a fifth. It was found that after administering 6 grams of hexamethylenetetramine to a dog, the urine only contained 2 grams.

Hexamethylenetetramine can behave as a mono- or di-basic base, but it has not been proved that it can form a tribasic salt with an inorganic acid, and a triborate cannot be prepared. Bayer's reagent for double linkings is not reduced by the base, and it probably does not contain an asymmetric carbon atom, for although it is partially burnt in the organism, the residue which is formed in the urine is optically inactive. Monobasicity is the chief objection to Duden and Scharff's constitutional formula.

Besides the compound $C_6H_{12}N_4,6HgCl_2$, the base also forms other very readily soluble compounds with salts. *Cystopurine*, or the compound with 2 mols. of sodium acetate and six of water, forms long, white, pointed crystals, and is a homogeneous substance which appears to possess certain advantages in respect to medicinal application; 1 part dissolves in 0·9 of cold water and 1·5 parts dissolve in 1 of warm water. Cystopurine may also be prepared directly from formalin, ammonia, and sodium acetate. E. W. W.

Mechanism of the Reaction in the Formation of α-Amino- and Imino-Acids. GEORGE STADNIKOFF (*Ber.*, 1907, **40**, 1014—1019. Compare Zelinsky and Stadnikoff, Abstr., 1906, i, 425).—If the assumption be made that an imino-nitrile is the product of a reaction between a hydroxy-nitrile (as a weak acid) and an amino-nitrile (as a base), the mechanism of the Strecker synthesis of α-amino-acids is understood; the formation of an imino-nitrile presupposes the presence of a hydroxy-nitrile as an intermediate product, and the whole process may be represented by the following example: $CH_3{\cdot}CHO,NH_3 + HCN = CH_3{\cdot}CHO + NH_4{\cdot}CN$; $NH_4{\cdot}CN + H_2O \rightleftharpoons NH_4{\cdot}OH + HCN$; $CH_3{\cdot}CHO + HCN = CH_3{\cdot}CH(OH){\cdot}CN$; $CH_3{\cdot}CH(OH){\cdot}CN + NH_3 = CH_3{\cdot}CH(NH_2){\cdot}CN + H_2O$; $CH_3{\cdot}CH(OH){\cdot}CN + CH_3{\cdot}CH(NH_2){\cdot}CN = H_2O + CH_3{\cdot}CH(CN){\cdot}NH{\cdot}CH(CN){\cdot}CH_3$.

The author proves that an imino-nitrile can be formed by the interaction of hydroxy-nitrile and amino-nitrile. Further, esters of amino-acids interact with hydroxy-nitriles to form imino-compounds, which, on hydrolysis, yield iminodicarboxylic acids.

Iminodipropionic acid was obtained in a 73·5% yield from α-aminopropionitrile, acetaldehyde, and potassium cyanide, and subsequent hydrolysis of the imino-nitrile thus formed; it is microcrystalline and has m. p. 235—236° (decomp.). The *nickel* and *copper* salts are described.

Iminodipropionic acid may also be obtained from ethyl *dl*-alanine hydrochloride, acetaldehyde, and potassium cyanide.

Iminotricarboxylic acid may be obtained from glutamic acid in an analogous manner. Its *copper* salt is described. A. McK.

Optically Active Modifications of Serine, *iso*Serine, and Diaminopropionic Acid. EMIL FISCHER and WALTER A. JACOBS (*Ber.*, 1907, **40**, 1057—1070. Compare Abstr., 1906, i, 807).—The benzoyl compounds of the amino-acids have been resolved by means of alkaloids, the brucine and quinine salts being used for *iso*serine and the quinidine and quinine salts for diaminopropionic acid. Since Neuberg and Silbermann (Abstr., 1905, i, 408) have connected *d*-glyceric acid with tartaric acid and hence with dextrose and so established its configuration, and E. Fischer (this vol., i, 192) has shown that the replacement of the amino-group by hydroxyl by means of nitrous acid is an optically normal reaction, it becomes possible to establish the configuration not only of serine but also of alanine. *d*-Serine yields *l*-glyceric acid and *l*-serine (the natural product) *d*-glyceric acid. Serine is converted by the action of hydrogen iodide into alanine (Fischer and

Leuchs, Abstr., 1902, i, 12), but at the high temperature racemisation takes place.

The *hydrochloride* of serine methyl ester is converted on shaking with acetyl chloride and phosphorus pentachloride into a well characterised, crystalline product, the *hydrochloride* of *ethyl β-chloro-a-aminopropionate*, $CH_2Cl\cdot CH(NH_2,HCl)\cdot CO_2Et$, which renders it possible to couple serine with other amino-acids.

Benzoyl-dl-iso*serine*, m. p. 151° (corr.), crystallises from water in pointed prisms aggregated in bunches, or from alcohol in microscopic needles; the *barium* salt forms aggregates of prisms and the sparingly soluble *copper* salt bunches of almost colourless plates. The *brucine* salt of benzoyl-l-*iso*serine separates slowly from a mixture of brucine and the above compound at 0°; benzoyl-*l*-iso*serine*, m. p. 107—109° (corr.), $[\alpha]_D^{20}$ $+10\cdot5°$, crystallises in right-angled, colourless prisms; the *barium* salt is characteristic and in acid solution has $[\alpha]_D^{20}$ $+11\cdot2°$. *l*-iso*Serine*, m. p. 199—201° (decomp.), $[\alpha]_D^{20}$ $-32\cdot58°$, forms large, colourless crystals.

Benzoyl-d-iso*serine*, $[\alpha]_D^{20}$ $-10\cdot12°$, and d-iso*serine*, $[\alpha]_D^{20}$ $+32\cdot44°$, are similar to the *l*-isomerides.

Dibenzoyl-*dl*-diaminopropionic acid was resolved by means of the *quinidine* salts, that of the *d*-compound being least soluble and crystallising in colourless, glistening needles. *Dibenzoyl*-d-*diaminopropionic acid*, m. p. 171—172° (corr.), $[\alpha]_D^{20}$ $-35\cdot76°$, crystallises from water in minute, rhombic plates and from ethyl acetate in stellate aggregates of prisms. d-*Diaminopropionic acid hydrochloride* becomes brown at 230°, m. p. 245° (corr.) (decomp.), $[\alpha]_D^{20}$ $+25°$, and forms bunches of long crystals. *Dibenzoyl* l-*diaminopropionic acid*, $[\alpha]_D^{20}$ $+35\cdot89°$, and l-*diaminopropionic acid*, $[\alpha]_D^{20}$ $-24\cdot98°$, have similar properties to the *d*-isomerides.

d-Serine was converted by the action of nitrous acid into the calcium salt of *l*-glyceric acid, $[\alpha]_D^{20}$ $+12\cdot94°$, crystallising in pointed prisms, whereas Frankland and Appleyard (Trans., 1893, **63**, 296) found $[\alpha]_D^{17}$ $-11\cdot66°$ for *d*-glyceric acid.

E. F. A.

New Compounds of Amino-Acids and Ammonia. PETER BERGELL (*Zeitsch. physiol. Chem.*, 1907, **51**, 207—212).—Several types of compounds of ammonia and amino-acids are known, but until the present research no compound has been described in which two amino-acid groups are united in an anhydride-like manner with their carboxyl groups linked by an ammonia group. The simplest representation of this would be *diglycinimide*, $NH(CO\cdot CH_2\cdot NH_2)_2$, and it was prepared as follows. Chloroacetamide is converted by heating with phosphoric oxide into the corresponding nitrile. This reacts with chloroacetic acid to form dichlorodiacetimide in which two chloroacetyl groups are united by an imino-group. By treatment with ammonia, using certain precautions, a *hydrochloride*,

$$HCl,NH_2\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot NH_2,$$

is obtained in crystalline form, m. p. 234—238°, and by careful treatment of this with silver oxide, the free base is obtained as a crystalline mass, m. p. 138°.

W. D. H.

Action of Absolute Nitric Acid on Heterocyclic Compounds. ANTOINE P. N. FRANCHIMONT (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 600—606).—Previous work by the author on this subject led to the formulation of the following rule. The hydrogen atom of the NH group is not attacked by absolute nitric acid when this group is situated between either two carbonyl groups or two saturated hydrocarbon residues, which, however, need not be CH_2 groups as stated wrongly by Harries (Abstr., 1903, i, 738), but when placed between two dissimilar groups, the hydrogen atom of the NH group is replaced by a nitro-group. It has now been found necessary to modify this rule, in that the direct nitration of heterocyclic compounds containing the NH group between a CO group and a saturated hydrocarbon residue depends on the configuration of the ring; for example, glycine anhydride, alanine anhydride, and ethyleneoxamide, all of which contain NH groups in the para-position in regard to each other, when treated with nitric acid yield not nitro-derivatives but nitrates.

W. H. G.

Compounds of Magnesium Bromide and Iodide with Derivatives of the Acids. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, i, 102—118. Compare Abstr., 1906, i, 552; this vol., i, 19, 386).—Walker and Johnson's compound, $KI,6COMe{\cdot}NH_2$ (Trans., 1905, 87, 1597), is probably a eutectic mixture, m. p. 54°, of potassium iodide and acetamide; amongst other reasons the existence of such a compound is very unlikely, owing to the fact that potassium iodide does not form hydrates or compounds with methyl alcohol.

Magnesium iodide forms with acetamide compounds similar to those formed by magnesium bromide, but they are less stable. The eutectic point of the system lies at 49° at the composition $MgI_2,15{\cdot}1COMe{\cdot}NH_2$; on further addition of magnesium iodide, the temperature rises until the *compound*, $MgI_2,6COMe{\cdot}NH_2$, m. p. 177°, separates. With acetonitrile, magnesium iodide forms the *compound* $MgI_2,6MeCN$, which crystallises from acetonitrile in long, colourless plates or stars, very hygroscopic and easily decomposed by water. It does not melt, but decomposes when the system contains 87% $MgI_2,6MeCN$ at 88°, after which the curve indicates the formation of a new substance, possibly $MgI_2,2MeCN$ or $MgI_2,4MeCN$. Magnesium bromide does not combine so readily with acetonitrile, but forms opaque solutions from which crystals of the *compound* $MgBr_2,3MeCN$, m. p. 132°, commence to separate above 88°. At the ordinary temperature another *substance*, probably $MgBr_2,4MeCN$, separates. With acetic anhydride, magnesium bromide yields the *compound* $MgBr_2,6OAc_2$, m. p. 136—137°. Acetyl chloride and magnesium bromide yield a *compound*, probably $MgBr_2,AcCl$, which decomposes without melting at low temperatures and does not dissolve in acetyl chloride. The *compound* $MgBr_2,BzCl$, with benzoyl chloride, crystallises better, but does not melt even at 200°. The solubility curves of all the compounds $MgX_2,6R$, in R (where R stands for acetamide, &c.), very much resemble the curves for $MgX_2,6H_2O$ in water, but the substances must be quite dry, as the least amount of moisture greatly increases the solubility. Composition-temperature curves for the substances investigated in this and previous papers are given. Z. K.

Reactions at Low Temperatures. II. Sulphides and Carbamates. Walter Peters (*Ber.*, 1907, 40, 1478—1482. Compare Abstr., 1906, i, 817).—The reactions between various bases and hydrogen sulphide or carbon dioxide in absolute ethereal solution at − 70° have been studied. The results are similar to those previously obtained with hydrogen cyanide. Hydrogen sulphide yields compounds with propylamine, diethylamine, triethylamine, tripropylamine, *as*-dimethylhydrazine, pentamethylenediamine, piperidine, and coniine. These compounds contain 2 molecules of base combined with 1 of hydrogen sulphide.

Carbon dioxide yields compounds with pyropylamine and *as*-dimethylhydrazine at the ordinary temperature, with piperidine at about − 15°, and with diethylamine, propylenediamine, and pentamethylenediamine at − 70°. The products are carbamates formed by the union of the dioxide (1 mol.) with 2 molecules of a monoamine or 1 molecule of a diamine, $2NH_2R + CO_2 = NHR{\cdot}CO{\cdot}ONH_3R$. Carbon dioxide does not combine with tertiary amines.

Ethyl glutaconate does not combine with iodine at − 70°, and at the same temperature trithioaldehyde and trithioacetone do not appear to combine with bromine. Phosphorus tri-iodide combines with iodine in carbon disulphide solution at − 70°, yielding the pentaiodide which is, however, excessively hygroscopic. J. J. S.

Preparation of Diurethane Derivatives of Dialkylmalonic Acids. Wilhelm Traube (D.R.-P. 179946).—The chlorides of the dialkylmalonic acids react with urethane only at temperatures above 100° to furnish diurethane derivatives in accordance with the following equation: $CEt_2(COCl)_2 + 2NH_2{\cdot}CO_2Et = 2HCl + CEt_2(CO{\cdot}NH{\cdot}CO_2Et)_2$.

This condensation is effected by heating the reagents either alone or in boiling xylene or cumene. G. T. M.

Calcium Cyanamide. Georg Bredig, W. Fraenkel, and E. Wilke (*Zeitsch. Elektrochem.*, 1907, 13, 69—75).—Powdered calcium carbide is heated with or without an admixture of 10% of other substances in an atmosphere of nitrogen, and the rate of absorption of nitrogen and also the quantity taken up after two hours are observed. At 800° the carbide alone absorbs about 3% of nitrogen in two hours; admixture of 10% of calcium chloride increases the absorption to 22%; 10% of barium chloride gives 12·5%. Lithium, sodium, and potassium chlorides give absorptions of about 17%, 12%, and 11% respectively, so that it appears that the acceleration of the reaction is greater the lower the atomic weight of the metal. Calcium fluoride, sulphate, oxide, and hydroxide cause little or no acceleration of the reaction; magnesia, coke-powder and sand do not accelerate, but sodium carbonate and sugar charcoal gave absorptions of 6% to 8% and 8% to 9% respectively.

Absorption begins at 750° with calcium carbide alone, whilst the mixtures with sodium or calcium chloride begin to take up nitrogen at 650°.

A set of experiments at 700° gave similar results; lithium chloride, however, gave a greater acceleration than calcium chloride.

The results show that the acceleration is not due (1) to the presence of oxygen salts of calcium, (2) to an initial rise of temperature, or (3) to an increase in the porosity of the mass. T. E.

Formation of Calcium Cyanamide. FRITZ FOERSTER and HANS JACOBY (*Zeitsch. Elektrochem.*, 1907, **13**, 101—107).—Curves are given showing the influence of time and temperature on the quantity of nitrogen absorbed by calcium carbide, both alone and mixed with calcium chloride or fluoride. With the commercial carbide (containing when powdered about 10% of calcium hydroxide) the absorption is slow and incomplete at temperatures below 1000°. Calcium fluoride accelerates the absorption, so that fairly complete conversion is attained in two hours at 900°. The effect of the quantity of the catalyst added is remarkable. The quantity of nitrogen absorbed in two hours at 800° increases with the quantity of calcium chloride added, the conversion being almost complete with 30% calcium chloride. With calcium fluoride, a maximum absorption of about 8% in two hours is reached with 5% of added fluoride at 800°, or 29% with 3% of fluoride at 900°; the addition of larger quantities of the fluoride diminishes the quantity of nitrogen absorbed.

The authors consider that the acceleration is due to partial fusion, owing to which any protective skin of calcium cyanamide is broken up and the unchanged carbide so exposed to the action of the nitrogen.

T. E.

Violent Explosions of Hydrocyanic Acid and the Nature of the Products formed thereby. EGIDIO POLLACCI (*Boll. Chim. Farm.*, 1907, **46**, 237—244).—The author describes several violent explosions of concentrated hydrocyanic acid solutions which have come under his notice. The explosions are accompanied by the formation of a black substance, which, when heated in a tube closed at one end, yields ammonia and hydrogen cyanide. This substance is apparently condensed or polymerised hydrogen cyanide, the ammonia evolved on heating being the result of the decomposition of part of the acid. When the substance is heated gradually in a test-tube, a sublimate of ammonium carbonate appears on the sides of the tube. The formation of this salt during the explosion is easily explained by assuming that cyanuric acid (or some other xanthic compound) is first formed. This acid would then decompose, giving cyanic acid, which, in presence of aqueous vapour, is rapidly transformed into ammonia and carbon dioxide: $HCNO + H_2O = NH_3 + CO_2$. T. H. P.

Method of Synthesis of Non-substituted β-Ketonic Nitriles. CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1907, **144**, 491—493).—When hydrolysed by sulphuric acid, phenylpropiolonitrile gives benzoylacetamide, $CH_2Bz{\cdot}CO{\cdot}NH_2$, whilst amylpropiolonitrile and hexylpropiolonitrile give amyl- and hexyl-propiolamides respectively.

In the former case, both the ·CN group and the acetylenic linking are attacked, whilst in the latter only the ·CN group is hydrolysed

(*Bull. Soc. chim.*, 1906, [iii], 35, 526). On the other hand, the hydrolysis of the condensation products of acetylenic nitriles with alcohols or phenols cannot easily be limited to the formation of β-ketonic nitriles (*loc. cit.*, p. 531).

The condensation products of acetylenic nitriles with amines (Abstr., 1906, i, 956), however, are easily hydrolysed by oxalic acid in ethereal solution with the formation of the corresponding β-ketonic nitrile and regeneration of the original amine. Thus β-amyl-β-piperidylacrylonitrile gives hexoylacetonitrile and piperidine:

$$C_5H_{11}\cdot C(C_5NH_{10})\colon CH\cdot CN + H_2O = C_5H_{11}\cdot CO\cdot CH_2\cdot CN + C_5NH_{11}.$$

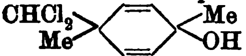
As the yields in this reaction and in the formation of the initial condensation derivative are nearly theoretical, the two processes form an excellent method of passing from acetylenic to β-ketonic nitriles. The latter are completely soluble in alkali hydroxide or carbonate solutions, from which they are reprecipitated by acids. The following are described.

Hexoylacetonitrile, $C_5H_{11}\cdot CO\cdot CH_2\cdot CN$, b. p. 126—128°/14 mm., D^{15} 0·9414; *heptoylacetonitrile*, $C_6H_{13}\cdot CO\cdot CH_2\cdot CN$, b. p. 137—141°/15 mm., D^{15} 0·9375. Benzoylacetonitrile, $COPh\cdot CH_2\cdot CN$, first prepared by Haller, was obtained similarly. E. H.

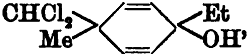
Constitution of Organo-Magnesium Compounds. Victor Grignard (*Bull. Soc. chim.*, 1907, [iv], 1, 256—262).—In reply to Tschelinzeff (this vol., i, 199), who adopts Baeyer and Villiger's formula for organo-magnesium compounds (Abstr., 1902, i, 355), mainly on the ground that it permits of the representation of the two isomeric forms of these compounds he has obtained, namely, $OR_2X\cdot MgR'$ and $ORR'X\cdot MgR$, the author points out that the formula proposed by himself (Abstr., 1903, i, 552) equally well accounts for the existence of isomerides, since it may be assumed that the two additional valencies of oxygen in oxonium compounds and of nitrogen in quinquevalent nitrogen derivatives have not the same value as the normal valencies, so that $R_2OR'\cdot MgX$ is not necessarily identical with $RR'O\cdot R\cdot MgX$, as has been supposed by Blaise (Abstr., 1906, i, 153), and instances are quoted in which interchanges of alkyl radicles of the type suggested have occurred (Blaise, Abstr., 1905, i, 111; Schmidlin, Abstr., 1906, i, 392; this vol., i, 26; and Grignard, Abstr., 1904, i, 494).

Blaise has asserted that in the case of amino-magnesium compounds the addition of water should lead to the production of an amine hydroxide and not to a hydrocarbon if Grignard's formula were correct. This view, it is suggested, is based on a misconception of the usual method of hydrolysis of organo-magnesium derivatives, which in this particular case may be represented as follows: $R_2R'R''N\cdot MgX + HO\cdot H = MgX\cdot OH + R_2R'R''N\cdot H$, the unstable substituted ammonium hydride thus formed decomposing immediately, forming the amine and hydrocarbon. The further objection of Blaise that the substituted ammonium iodides do not react with magnesium, has, in the author's opinion, little weight, since the quaternary ammonium radicle has little in common with an alkyl radicle. Incidentally it is pointed out that this non-reactivity of the substituted ammonium iodides with magnesium contradicts Tschelinzeff's view that in the formation of organo-magnesium compounds the ether or the tertiary amine dissociates the alkyl haloid, forming substances of the type $R'OR_2X$ and $RR'R''R'''N{\cdot}X$, with which the magnesium then reacts (Abstr., 1905, i, 40). Tschelinzeff's suggestion that by analogy with other oxonium and ammonium compounds organo-magnesium derivatives should be regarded as having the haloid atom attached directly to the oxygen or nitrogen is regarded as unlikely, since they decompose with the production of a magnesium haloid salt, whence there is reason to believe, with Abegg (Abstr., 1906, i, 57), that the radicle MgX behaves as the positive portion of the molecule; the organic residue being the negative portion. With regard to the constitution of the organo-magnesium compounds containing a second molecule of ether the author thinks there is less objection to the formula proposed by Tschelinzeff (Abstr., 1906, i, 241) than to that used by Zelinsky (Abstr., 1903, i, 802) and by Blaise (Abstr., 1905, i, 111). T. A. H.

Alkylidenedihydrobenzenes. KARL AUWERS (*Annalen*, 1907, **352**, 219—272. Compare Abstr., 1903, i, 100, 620; 1904, i, 26; 1905, i, 434).—It has been shown previously that the alcohols,



and



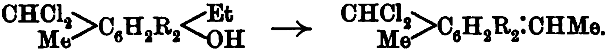
formed from 4-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene by Grignard's reaction, readily lose water and yield unstable products which undergo transformation into the benzene derivatives, $C_6H_4Me{\cdot}CH_2{\cdot}CHCl_2$ and $C_6H_4Me{\cdot}CHMe{\cdot}CHCl_2$ respectively. The work described in the two following papers, to which this is a general introduction, was undertaken to determine the constitution of the intermediate products, and by applying Grignard's reaction to the condensation products of chloroform and *as-m*-xylenol, *as-o*-xylenol, and *ψ*-cumenol to ascertain if the loss of water takes place with hydroaromatic alcohols derived from homologues of *p*-cresol.

The configuration of the condensation product of chloroform with *p*-cresol, as 4-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene is confirmed by the formation of *β*-chloromethylacrylic acid, a decomposition product of methyldichloromethylmalonic acid, on oxidation of the ketone with potassium permanganate.

The constitutions of the unstable compounds formed by loss of water from the hydroaromatic alcohols, $CHCl_2{\cdot}C_6H_2R_2R'Me{\cdot}OH$ ($R = H$ or Me; $R' = Me$ or Et), derived from the above three homologues of *p*-cresol, and of the benzene transformation products are discussed. By identification of the aldehydes and ketones formed by elimination of hydrogen chloride and oxidation of the resulting chlorostyrenes, $C_6H_2R_2Me{\cdot}CH{:}CHCl$ and $C_6H_2R_2Me{\cdot}CMe{:}CHCl$ ($R = H$ or Me), the transformation products are shown to be homologues of *p*-*ββ*-dichloroethyltoluene, $C_6H_2R_2Me{\cdot}CH_2{\cdot}CHCl_2$, and of *p*-dichloro*iso*propyltoluene, $C_6H_2R_2Me{\cdot}CHMe{\cdot}CHCl_2$, respectively.

Of the hydroaromatic alcohols described, those derived from *p*-cresol, *as-o*-xylenol, and *ψ*-cumenol, having $R' = Et$, lose water most easily, whilst the alcohols derived from *as-m*-xylenol, having $R' = Et$, and from *as-o*-xylenol, with $R' = Me$, are the most stable. Most, if not all, of these hydroaromatic alcohols occur in two modifications which differ in melting point and solubility, and are probably *cis*- and *trans*-forms.

The formation of the unstable intermediate products and their transformation into the stable benzene derivatives can be followed by observation of the change in the angle of refraction which is least for the intermediate compounds. It was shown previously (Abstr., 1905, i, 445) that successive action of phosphorus pentachloride and water on 4-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene leads to the formation of *p*-chloro-*o*-tolualdehyde; it is found now that the unstable products derived from *p*-cresol and *ψ*-cumenol are converted analogously by the action of sulphuric acid into 2 : 4-dimethyl- and 2 : 3 : 4 : 5-tetramethyl-benzaldehydes respectively. From this it is argued that the intermediate compounds must be alkylidene*cyclo*hexadienes, the relation of which to the hydroaromatic alcohols is expressed by the formula: $\begin{matrix}CHCl_2\\Me\end{matrix}\!>C_6H_2R_2<\!\begin{matrix}Me\\OH\end{matrix} \rightarrow \begin{matrix}CHCl_2\\Me\end{matrix}\!>C_6H_2R_2{:}CH_2$ and $\begin{matrix}CHCl_2\\Me\end{matrix}\!>C_6H_2R_2<\!\begin{matrix}Et\\OH\end{matrix} \rightarrow \begin{matrix}CHCl_2\\Me\end{matrix}\!>C_6H_2R_2{:}CHMe$. It is shown that the molecular refractions of the intermediate compounds are in agreement with those calculated from these alkylidene formulæ.



The general chemical and physical properties of the alkylidene*cyclo*hexadienes are discussed, compared with those of other analogous and closely related compounds, and shown to support the above conclusions as to the constitution of the compounds in question.

In the following two papers a large number of refractive indices are given, of which only the limiting values of n_D are quoted.

G. Y.

Derivatives of Alkylidenedihydrobenzenes from *p*-Cresol. KARL AUWERS and M. HESSENLAND (*Annalen*, 1907, **352**, 273—287. Compare Auwers and Keil, Abstr., 1903, i, 100, 620; 1905, i, 445; and preceding abstract).—On extraction with light petroleum, the resin insoluble in aqueous alkalis, formed in the preparation of 4-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene, yields p-*tolyl orthoformate*, $CH(O{\cdot}C_6H_4Me)_3$, crystallising in colourless prisms, m. p. 112°.

1-Hydroxy-1 : 4-dimethyl-4-dichloromethyl*cyclo*hexadiene is found now to exist in two stereoisomeric modifications, one of which has been described (Abstr., 1903, i, 620); the second form separates from light petroleum in stout, transparent crystals, m. p. 65°. No difference could be observed in the stabilities of the two modifications. When heated with light petroleum at 45° in a current of hydrogen, this hydroaromatic alcohol yields 4-*methyl*-4-*dichloromethyl*-1-*methylene*cyclo*hexadiene*, $CHCl_2{\cdot}C_6H_4Me{:}CH_2$, which is obtained as a yellow oil, $D_4^{14·2}$ 1·1800, $n_D^{14·1}$ 1·55844, $n_D^{18·5}$ 1·56109, commences to polymerise after one to two days at the ordinary temperature, and at 70—80° is transformed into *p*-*ββ*-dichloroethyltoluene, b. p. 114—116°/14 mm. or 129—132°/23 mm., D_4^{14} 1·1734, $D_4^{22·4}$ 1·1638, n_D^{14} 1·53940, $n_D^{21·6}$ 1·53610. This is converted by boiling alcoholic potassium hydroxide into *β*-chloro-*p*-methylstyrene (Abstr., 1904, i, 27), b. p. 99—102°/14 mm. or 129—132°/39 mm., $D_4^{28·7}$ 1·0565, $n_D^{26·8}$ 1·56635.

The action of chlorine on 4-methyl-4-dichloromethyl-1-methylene-

*cyclo*hexadiene in carbon tetrachloride solution cooled by ice, leads to the formation of a mixture of tri- and di-chloro-compounds. The *trichloro*-compound, $C_6H_4Me{\cdot}CH_2{\cdot}CCl_3$?, forms a colourless oil, b. p. 135—142°/8—9 mm., and when boiled with alcoholic potassium hydroxide yields a light yellow *oil*, which contains chlorine, and is volatile with steam, together with *p*-tolylacetic acid.

2 : 4-Dimethylbenzaldehyde, formed by heating 4-methyl-4-dichloromethyl-1-methylene*cyclo*hexadiene with 80% sulphuric acid at 80—90°, is obtained as a yellow oil; it yields a *semicarbazone* crystallising in small prisms, m. p. 225—227°, and is oxidised by permanganate to 2 : 4-dimethylbenzoic acid.

*4-Methyl-4-dichloromethyl-1-ethylidene*cyclo*hexadiene*,

$$CHCl_2{\cdot}C_6H_4Me{:}CHMe,$$

formed by carefully heating 1-hydroxy-4-methyl-4-dichloromethyl-1-ethyl*cyclo*hexadiene (Abstr., 1905, i, 434), or by shaking it with anhydrous formic acid, is obtained as a yellow oil, $D_4^{15·3}$ 1·1669—1·1696, $n_D^{15·3}$ 1·56343. *p*-Dichloro*iso*propyltoluene, b. p. 123—125°/13 mm., $D_4^{14·6}$ 1·1534, D_4^{23} 1·1519, $n_D^{14·6}$ 1·53732, $n_D^{22·7}$ 1·53441. *β*-Chloro-*a*-*p*-dimethylstyrene, b. p. 106—108°/10 mm., D_4^{20} 1·0580, n_D^{19} 1·55714, n_D^{23} 1·55494. G. Y.

Alkylidenedihydrobenzenes from *as-m*-Xylenol, *as-o*-Xylenol, and *ψ*-Cumenol. KARL AUWERS and A. KÖCKRITZ (*Annalen*, 1907, **352**, 288—321. Compare Abstr., 1900, i, 160; 1902, i, 218; 1903, i, 100; and preceding abstract).—*Derivatives of* as-m-*xylenol*.—*4-Hydroxy-1 : 3 : 4-trimethyl-1-dichloromethyl*cyclo*hexadiene*, $C_{10}H_{14}OCl_2$, formed by the action of magnesium methyl iodide on 4-keto-1 : 3-dimethyl-1-dichloromethyl*cyclo*hexadiene, crystallises in transparent, monoclinic prisms, m. p. 82—83°, and decomposes gradually at the ordinary temperature, forming a resinous mass. When heated with ether at 45°, or shaken with formic acid at the laboratory temperature, it yields 1 : 3-*dimethyl-1-dichloromethyl-4-methylene*cyclo*hexadiene*, which is transformed at 80—90° into 1 : 3-*dimethyl-4-ββ-dichloroethylbenzene*, $C_{10}H_{12}Cl_2$, b. p. 124—126°/12 mm. or 136—138°/17 mm., $D_4^{14·2}$ 1·1507, D_4^{19} 1·1574, $n_D^{7·5}$ 1·54457, $n_D^{19·5}$ 1·53927. On prolonged boiling with alcoholic potassium hydroxide, this is converted into *β-chloro*-1 : 3-*dimethylstyrene*, $C_6H_3Me_2{\cdot}CH{:}CHCl$, which is obtained as a colourless oil, b. p. 117—120°/14 mm., $D_4^{23·9}$ 1·0466, $n_D^{23·9}$ 1·56351, and on oxidation with permanganate in aqueous acetone solution yields 2 : 4-dimethylbenzaldehyde, formed also by Gattermann's method from *m*-xylene. It forms a *semicarbazone*, crystallising in leaflets, m. p. 226°, and is oxidised to 2 : 4-dimethylbenzoic acid.

*4-Hydroxy-1 : 3-dimethyl-1-dichloromethyl-4-ethyl*cyclo*hexadiene*, $C_{11}H_{18}OCl_2$, formed by the action of magnesium ethyl iodide on 4-keto-1 : 3-dimethyl-1-dichloromethyl*cyclo*hexadiene, crystallises in slender needles or stout, transparent prisms, m. p. 85—85·5°; a urethane could not be obtained with phenylcarbimide, diphenylcarbamide being formed. 1 : 3-*Dimethyl-1-dichloromethyl-4-ethylidene*cyclo*hexadiene*, $C_{11}H_{14}Cl_2$, is obtained as a mobile, colourless oil, D_4^{21} 1·1393, n_D^{9} 1·56605, $n_D^{22·9}$ 1·55917. 1 : 3-*Dimethyl-4-dichloro*iso*propylbenzene*, formed from the preceding substance at 120°, is a colourless oil, b. p. 135—137°/

11 mm. or 143—144°/16 mm., $D_4^{14\cdot9}$ 1·1396, $D_4^{22\cdot6}$ 1·1345, n_D^{7} 1·54212, $n_D^{22\cdot6}$ 1·53619. *β-Chloro-a-2 : 4-trimethylstyrene*, $C_6H_3Me_2\cdot CMe\colon CHCl$, is a colourless oil, b. p. 112—114°/16 mm. or 124—125°/24 mm. Reduction of the dichloro-compound with sodium and alcohol leads to the formation of 1 : 3-dimethyl-4-*iso*propylbenzene, which on bromination is converted into tetrabromo-*m*-xylene, m. p. 248° (241° : Fittig and Bieber, *Annalen*, 1870, **156**, 236).

A *polymeric modification* of 1 : 3-dimethyl-1-dichloromethyl-4-ethylidene*cyclo*hexadiene, crystallising in nacreous leaflets, m. p. 183—184°, is formed from the corresponding hydroaromatic alcohol in four months at the winter temperature, or more rapidly from the unimolecular ethylidene compound.

Derivatives of as-o-*xylenol.*—4-*Hydroxy*-1 : 2 : 4-*trimethyl*-1-*dichloromethyl*cyclo*hexadiene*, $C_{10}H_{14}OCl_2$, crystallises in transparent, monoclinic prisms, m. p. 79·5°. 1 : 2-*Dimethyl*-4-*ββ-dichloroethylbenzene* is a colourless oil, b. p. 126—128°/9 mm. or 134—136°/11 mm., $D_4^{14\cdot2}$ 1·1513, D_4^{21} 1·1428, $n_D^{14\cdot2}$ 1·54144, n_D^{21} 1·53789. The intermediate methylene compound could not be isolated. *β-Chloro*-3 : 4-*dimethylstyrene* is an aromatic, colourless oil, b. p. 126—128°/14 mm., and on oxidation with permanganate in aqueous acetone solution yields 3 : 4-*dimethylbenzaldehyde*, which is formed also directly from *o*-xylene; the *semicarbazone*, $C_{10}H_{13}ON_3$, crystallises in needles, m. p. 224° or, when quickly heated, 227—228°. On further oxidation, the aldehyde yields 3 : 4-dimethylbenzoic acid. The *polymeride* of the methylene compound crystallises from alcohol in flat prisms, m. p. 153—154°; the melting point sinks with repeated recrystallisations.

4-*Hydroxy*-1 : 2-*dimethyl*-1-*dichloromethyl*-4-*ethyl*cyclo*hexadiene* commences to decompose immediately at the laboratory temperature. 1 : 2-*Dimethyl*-1-*dichloro*-4-*ethylidene*cyclo*hexadiene*, $C_{11}H_{14}Cl_2$, was obtained as an impure oil, D_4^{19} 1·1761. 1 : 2-*Dimethyl*-4-*ββ-dichloro*iso*propylbenzene* is a transparent oil, b. p. 135—140°/14 mm., $D_4^{20\cdot3}$ 1·1352, n_D^{21} 1·53837. β-Chloro-a-3 : 4-trimethylstyrene solidifies in a freezing mixture; m. p. 22°, b. p. 128°/14 mm., $D_4^{22\cdot8}$ 1·0490, $n_D^{22\cdot8}$ 1·55745, and on oxidation yields 3 : 4-dimethylacetophenone, which forms a *semicarbazone*, $C_{11}H_{15}ON_3$, stout, white needles, m. p. 233—234°.

Derivatives of ψ-cumenol.—4-*Hydroxy*-1 : 2 : 4 : 5-*tetramethyl*-1-*dichloromethyl*cyclo*hexadiene* crystallises from light petroleum in long needles, m. p. 76—78°, decomposes gradually, forming a yellow oil, and gives with fuming nitric acid a dark blue coloration changing to carmine. 1 : 2 : 5-*Trimethyl*-1-*dichloromethyl*-4-*methylene*cyclo*hexadiene*, D_4^{14} 1·1484, D_4^{19} 1·1446, n_D^{14} 1·56096, $n_D^{18\cdot8}$ 1·55920. 1 : 2 : 5-*Trimethyl*-4-*ββ-chloroethylbenzene*, a colourless oil, solidifying at low temperatures, m. p. 22°, b. p. 134—136°/10 mm. or 143—145°/13 mm., D_4^{17} 1·1357, n_D^{16} 1·54252. *β-Chloro*-2 : 4 : 5-*trimethylstyrene*, a colourless oil, b. p. 133—134°, $D_4^{21\cdot8}$ 1·0429, $n_D^{21\cdot8}$ 1·56680; on oxidation, this yields 2 : 4 : 5-trimethylbenzaldehyde and 2 : 4 : 5-trimethylbenzoic acid. The *semicarbazone* of the aldehyde, $C_{11}H_{15}ON_3$, crystallises in flat prisms, m. p. 243—244°.

4-*Hydroxy* - 1 : 2 : 5-*trimethyl*-1-*dichloromethyl* - 4 - *ethyl*cyclo*hexadiene* and 1 : 2 : 5-*trimethyl*-1-*dichloromethyl*-4-*ethylidene*cyclo*hexadiene* were not isolated in a state of purity. 1 : 2 : 5-*Trimethyl*-4-*dichloro*iso-

propylbenzene crystallises from light petroleum or methyl alcohol in slender needles, m. p. 43—44°, b. p. 135—137°/10 mm. or 155—157°/16 mm., D_4^{15} 1·1321, $D_4^{21\cdot9}$ 1·1263, $n_D^{21\cdot9}$ 1·53812. *β-Chloro-α-*2 : 4 : 5-*tetramethylstyrene* is a colourless oil, b. p. 126—127°/16 mm. or 131—133°/24 mm., D_4^{20} 1·0341, n_D^{20} 1·54182, and after oxidation yields a *semicarbazone*, $C_{12}H_{17}ON_3$, rectangular plates, m. p. 204°, identical with that formed from 2 : 4 : 5-trimethylacetophenone prepared from ψ-cumene and acetyl chloride. 1 : 2 : 5-*Trimethyl*-4-iso*propylbenzene*, prepared by reduction of the dichloro-compound with sodium and alcohol, b. p. 221·5—223·5°, D_4^{21} 0·8795, n_D^{21} 1·50648. The *polymeric modification* of the methylene compound, $(C_{11}H_{14}Cl_2)_2$, is formed from the unimolecular compound in the course of some days at the ordinary temperature; it crystallises in small needles, m. p. 132—138°, or after partial oxidation with permanganate, 151—157°. When reduced with sodium and alcohol, it yields durene. The action of cooled, concentrated sulphuric acid on the uni- or bi-molecular methylene compound leads to the formation of an *aldehyde* which is oxidised rapidly by air, forming durenecarboxylic [prehnitenecarboxylic] acid (Meyer and Molz, Abstr., 1897, i, 476). The *semicarbazide*, $C_{12}H_{17}ON_3$, crystallises in long, white needles, m. p. 229—230°. Dinitroprehnitene, m. p. 176°, is formed by the action of fuming nitric acid on prehnitene or prehnitenecarboxylic acid. G. Y.

Derivatives of *o*- and *p*-*tert*.-Butyltoluenes. J. Kozak (*Bull. Acad. Sci. Cracow*, 1906, 407—417).—This is a study of the dyes obtained by the action of dehydrating agents on the condensation products of maleic anhydride with *o*- and *p*-*tert*.-butyltoluenes (v. Pechmann, Abstr., 1882, 1074; Marchlewski, Abstr., 1903, i, 667).

The action of bromine on *tert*.-butylbenzene in presence of iodine leads to the formation of a mixture of *o*- and *p*-bromo-derivatives which are converted by Fittig's reaction into o- and p-tert.-*butyltoluenes*; these are separated by fractional distillation.

o-tert.-*Butyltoluene*, b. p. 170—170·5°/743·1 mm., n_D^{17} 1·49423.

p-tert.-*Butyltoluene*, b. p. 192—192·5°/742 mm., n_D^{17} 1·493565.

4-*Methyl*-3-tert.-*butylbenzoyl*- or 3-*methyl*-4-tert.-*butylbenzoyl-acrylic acid*, $C_4H_9\cdot C_6H_3Me\cdot CO\cdot CH{:}CH\cdot CO_2H$, formed by the action of aluminium chloride and maleic anhydride on *o*-*tert*.-butyltoluene, cooled by ice-water, crystallises in yellow, monoclinic needles, m. p. 123—124°, and when heated with acetic anhydride yields a *dye*, $C_{15}H_{16}O_2$, which forms dark bronze crystals, m. p. 320—326°, sublimes below its melting point, has a yellowish-red fluorescence when dissolved in organic solvents, and dissolves in concentrated sulphuric acid to a blue solution becoming red and then yellowish-brown when heated. The absorption spectrum of the solution in toluene shows two dark bands in the yellow and green, λ 559—541 and λ 518—502 respectively.

The condensation of maleic anhydride with *p*-*tert*.-butyltoluene leads to the formation of two *methyl*-tert.-*butylbenzoylacrylic acids*,

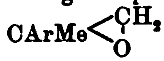
$$C_4H_9\cdot C_6H_3Me\cdot CO\cdot CH{:}CH\cdot CO_2H,$$

of which the one crystallising first from water, termed the *α-acid*, forms yellow needles or prisms, m. p. 133—134°. The more soluble *β-acid* crystallises in more intensely yellow needles or prisms, m. p. 115—117°.

The *dye*, obtained by the action of acetic anhydride on the *a*-acid, crystallises in almost black needles, m. p. 198—208°, is fluorescent in dilute solution, and dissolves to a blue solution in concentrated sulphuric acid.

The *dye*, $C_{15}H_{16}O_2$, formed from the β-acid, crystallises in reddish-brown needles, m. p. 202—206°, is fluorescent in dilute solution, and forms a violet solution in concentrated sulphuric acid.

The absorption spectra of the two dyes derived from *p-tert.*-butyltoluene show the same two bands as observed in that of the dye derived from *o-tert.*-butyltoluene. G. Y.

Benzene Hydrocarbons containing a ψ-Allyl Side-Chains: Methoethenylbenzene and its Homologues. Studies in Molecular Migration. II. Molecular Transpositions Accompanying the Transformation of a-Glycols and their Derivatives into Aldehydes and Ketones. Marc Tiffeneau (*Ann. Chim. Phys.*, 1907, [viii], 10, 322—378. Compare Abstr., 1906, i, 724, 965; this vol., i, 130).—This paper opens with a long theoretical introduction and concludes with a general review of the experimental results described in Parts I (this vol., i, 304) and II. It was found previously (*loc. cit.*) that the halohydrins, formed by addition of hydrogen oxyhaloids to ψ-allylbenzenes, lose the hydrogen haloid when treated with alkalis, forming ethylene oxides which on distillation undergo simple change into aldehydes: $\mathrm{OH{\cdot}CArMe{\cdot}CH_2X} \longrightarrow$  $\mathrm{CArMe}<\begin{smallmatrix}\mathrm{CH_2}\\ | \\ \mathrm{O}\end{smallmatrix}$ $\longrightarrow \mathrm{CHArMe{\cdot}CHO}$, whereas when treated with certain metallic oxides or salts, such as mercuric oxide or silver nitrate, the substance obtained is a product of intramolecular change: $\mathrm{OH{\cdot}CArMe{\cdot}CH_2X} \longrightarrow \mathrm{CH_2Ar{\cdot}COMe}$. As such intramolecular wandering of groups has been described only in isolated cases, the phenomenon has been studied now systematically in that of the *a*-glycols and their derivatives, the halohydrins, the magnesium derivatives of the halohydrins, and the ethylene oxides.

With regard to the manner in which they are transformed into aldehydes or ketones, *a*-glycols and their derivatives fall into two classes: (*a*) these in which the transformation is accompanied by a change in the position of a hydrogen atom, and (*b*) those in which the transformation is accompanied by a change in the structure of the carbon nucleus resulting from a wandering of a carbon radicle. It is considered that the first stage in the transformation of an *a*-glycol or derivative of an *a*-glycol into an aldehyde or ketone leads always to the formation of an unstable intermediate form of the type

$$\cdot\mathrm{CRR'{\cdot}CR''R'''{\cdot}O}\cdot,$$

the further change of which depends on the nature and position of the substituting groups.

Class (*b*) includes all tetra-substituted *a*-glycols, halohydrins, magnesium derivatives of the halohydrins which are formed by addition of organo-magnesium compounds to *a*-chloroketones, and ethylene oxides, and all polysubstituted aromatic α-glycols, halohydrins, and magnesium derivatives of halohydrins which have an aromatic substituting group attached to the carbon atom carrying the oxygen atom of the hypothetical unstable intermediate substance.

All other α-glycols, halohydrins, and magnesium derivatives, as also all mono-, di-, and tri-substituted ethylene oxides, are included in class (*a*).

The transformation of tetrasubstituted α-glycols, the pinacolin transformation, differs from the formation of aldehydes or ketones from mono-, di- or tri-substituted α-glycols in that it can take place only if accompanied by intramolecular change in the position of one of the substituting groups, and that all the groups present are capable of undergoing the intramolecular transposition, which takes place, however, more readily with an aromatic group than with an aliphatic group and more readily with methyl than with ethyl.

The experimental part of this paper is chiefly a detailed account of work published previously.

β-Phenylpropylene αβ-glycol, $OH\cdot CPhMe\cdot CH_2\cdot OH$, formed by the action of baryta on ψ-allylbenzene dibromide, crystallises in needles, m. p. 42—43°, b. p. 160—162°/26 mm., and when boiled with dilute sulphuric acid yields hydratropaldehyde together with small amounts of Stoermer's anhydride (Abstr., 1906, i, 581).

β-p-*Tolylpropylene αβ-glycol*, $C_7H_7\cdot CMe(OH)\cdot CH_2\cdot OH$, prepared by the action of baryta on *p*-ψ-allyltoluene dibromide, or on *p*-toluoylcarbinol or its acetate, crystallises in needles, m. p. 36°, b. p. 175—180°/15 mm., and when boiled with dilute sulphuric acid yields *p*-methylhydratropaldehyde, which forms a semicarbazone, m. p. 152° (159—160°: Darzens, Abstr., 1905, i, 116).

αα-Diphenylethylene glycol, $OH\cdot CPh_2\cdot CH_2\cdot OH$, m. p. 122°, formed by the action of magnesium phenyl bromide on ethyl glycollate, when boiled with sulphuric acid yields diphenylacetaldehyde.

α-Phenylpropylene αβ-glycol, formed by the action of potassium carbonate on phenylene dibromide, is converted by boiling sulphuric acid into phenylacetone.

Styrene oxide is very stable towards hydrolysing agents. ψ-Allylphenyl oxide, when boiled with sulphuric acid, yields α-phenylpropaldehyde, but is stable towards silver nitrate.

The structure of the iodohydrin derived from styrene,

$$OH\cdot CHPh\cdot CH_2I$$

(Bougault, Abstr., 1900, i, 641), is established by its conversion into *sec.*-phenylethyl alcohol by successive acetylation, reduction, and hydrolysis, or into dimethylphenacylamine by the action of dimethylamine. The isomeric *iodohydrin*, $OH\cdot CH_2\cdot CHPhI$, formed by the action of hydrogen iodide on styrene oxide, crystallises in spangles, m. p. 79°.

p-Methoxystyrene, $OMe\cdot C_6H_4\cdot CH{:}CH_2$, prepared by dehydration by Klage's method of *p*-methoxyphenylmethylcarbinol (Abstr., 1904, i, 1001), is converted by the action of mercuric oxide and iodine into p-*methoxyphenylacetaldehyde*, $OMe\cdot C_6H_4\cdot CH_2\cdot CHO$, b. p. 255—256°, D^0 1·140, which yields an oxime, m. p. 121° (112°: Bouveault, *loc. cit.*), and a *semicarbazone*, m. p. 181—182°. Reduction of this aldehyde with zinc and acetic acid leads to the formation of p-*methoxyphenylethyl acetate*, b. p. 156—157°/11 mm. or 277—278°/760 mm., D^0 1·101.

Hydratropaldehyde is formed by the successive action of mercuric oxide and iodine and potassium iodide and sodium hydrogen sulphite on phenylpropylene; it reacts with magnesium phenyl bromide forming the alcohol, $\mathrm{CHPhMe\cdot CHPh\cdot OH}$. The constitution,

$$\mathrm{OH\cdot CHPh\cdot CHMeI},$$

has been established for the iodohydrin obtained from phenylpropylene, by its conversion into phenylethylcarbinyl acetate, and into β-dimethylamino-α-phenylpropane-α-ol, $\mathrm{OH\cdot CHPh\cdot CHMe\cdot NMe_2}$.

α-Phenyl*iso*valeraldehyde forms a *semicarbazone*, m. p. 140°.

αβ-Diphenylpropylene (Klages, Abstr., 1902, i, 668) is formed by the action of magnesium phenyl bromide on phenylacetone.

β-n-*Propylcinnamic acid*, $\mathrm{CPhPr^{\alpha}\!:\!CH\cdot CO_2H}$, b. p. 198—201°/18 mm., obtained on hydrolysis of its *ethyl* ester, prepared by condensation of phenylbutanone with ethyl iodoacetate, and distillation under the ordinary pressure, loses carbon dioxide when boiled, yielding β-phenyl-Δ^{α}-amylene, which forms a liquid *dibromide*.

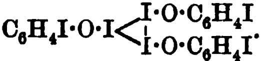
αα-Diphenylethyl alcohol, $\mathrm{CPh_2Me\cdot OH}$, m. p. 80—81°, b. p. 175—180°/20 mm., is obtained from αα-diphenylethylene, and, by way of the iodohydrin, yields deoxybenzoin.

*α-Phenyl-α-*p*-tolylethylene*, $\mathrm{C_7H_7\cdot CPh\!:\!CH_2}$, b. p. 145—146°/6 mm. or 160—161°/11 mm., formed by repeated distillation under the ordinary pressure of the corresponding carbinol, yields *p*-tolylacetophenone. *γ-Phenyl-Δ^{β}-amylene*, $\mathrm{CPhEt\!:\!CHMe}$, b. p. 197—199°, D^0 0·9321, formed by the action of oxalic acid on phenyldiethylcarbinol prepared by treating ethyl benzoate with magnesium ethyl bromide, yields *methylbenzyl ethyl ketone*, $\mathrm{CHPhMe\cdot COEt}$, b. p. 222—225°, D^0 0·982; the *semicarbazone*, m. p. 172°.

Benzyl ethyl ketone, formed from the *additive* compound of magnesium phenyl bromide and chloroacetophenone, yields a *semicarbazone*, $\mathrm{C_{11}H_{15}ON_3}$, m. p. 146°. G. Y.

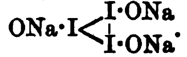
Iodation of Phenol in a Borax Solution, and the Production of ψ-Iodosoiodobenzene. E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1204—1210).

—The iodine compounds of phenol, β- and α-naphthol, thymol, pyrogallol, and sodium salicylate form precipitates insoluble in borax. The iodation product of phenol crystallising from chloroform in pink needles, m. p. 144—145°, has none of the properties of iodosoiodobenzene, and is most probably *ψ-iodosoiodobenzene*,



$\mathrm{C_6H_4I\cdot O\cdot I}\!<\!\begin{matrix}\mathrm{I\cdot O\cdot C_6H_4I}\\ |\\ \mathrm{I\cdot O\cdot C_6H_4I}\end{matrix}$.

In concentrated sodium hydroxide it forms a turbid solution, probably due to the formation of the elementary molecule $\mathrm{OI\cdot C_6H_4I}$, but in attempting to isolate the latter, the original substance is again obtained. With nitrodiazobenzene chloride in alkaline solution it forms a yellow *azo-compound*, $\mathrm{NO_2\cdot C_6H_4\cdot N\!:\!N\cdot C_6H_3I\cdot ONa}$, sodium iodide and iodate being liberated, but on attempting to estimate the quantity of iodate in the solution by means of hydrazine sulphate, only half the theoretical volume of nitrogen is liberated; the reason for this is not clear, possibly the iodate reacts further with the azo-compound in solution. Iodine in borax solution behaves with sodium thiosulphate differently from ordinary free iodine, also when such a solution is acted on by hydrazine sulphate the nitrogen liberated is the theoretical quantity which would be necessary if all the iodine formed the compound



$ONa\cdot I<\begin{matrix} I\cdot ONa \\ | \\ I\cdot ONa \end{matrix}$.

Z. K.

Oxidation of *o*-Nitrotoluene in the Side-Chain with Manganese Dioxide and Sulphuric Acid. Badische Anilin- & Soda-Fabrik (D.R.-P. 179589).—The extent to which manganese dioxide and sulphuric acid oxidise *o*-nitrotoluene depends on the concentration of the acid. *o*-Nitrotoluene, when heated in an autoclave with 2 parts of finely-powdered manganese dioxide and 10 parts of sulphuric acid of 30—40° Bé. at 140—165° for two to three hours, is converted mainly into *o*-nitrobenzaldehyde, only a small proportion of *o*-nitrobenzoic acid being formed. The pressure is regulated so as not to exceed 10 atmospheres. When acid of 50—60° Bé. is employed and the temperature is maintained at 135—145°, *o*-nitrobenzoic acid becomes the chief product. These oxidations may be performed under the ordinary pressure, but more concentrated acid is required.

G. T. M.

Oxidation of Naphthalene to Phthalonic Acid by Alkaline Solutions of Permanganate. R. Arthur Daly (*J. Physical Chem.*, 1907, 11, 93—106).—Experiments have been made to ascertain which of the numerous possible intermediate compounds may be regarded as actual stages in the oxidation of naphthalene to phthalonic by alkaline permanganate solutions. For this purpose the rates of oxidation of naphthalene, homophthalic acid, *o*-carboxymandelic acid, *o*-carboxybenzoylacetic acid, and of *a*- and *β*-naphthaquinones by decinormal permanganate solution containing sodium hydrogen carbonate have been measured at 40°. From the slow rate of oxidation of homophthalic and *o*-carboxymandelic acids, the conclusion is drawn that these cannot be intermediate products in the formation of phthalonic acid from naphthalene, *o*-carboxybenzoylacetic acid, or the naphthaquinones.

In a similar manner it seems probable that *β*-naphthaquinone does not represent a stage in the oxidation of naphthalene, whereas *o*-carboxybenzoylacetic acid and *a*-naphthaquinone are possible intermediate substances.

H. M. D.

Course of the Oxidation of *β*-Naphthaquinone to Phthalic Acid. Maitland C. Boswell (*J. Physical Chem.*, 1907, 11, 119—131. Compare Daly, preceding abstract).—Information in regard to the intermediate products formed in the oxidation of *β*-naphthaquinone to phthalic acid by acid dichromate solutions has been sought by a comparative study of the rates of oxidation of the quinone and several possible intermediate substances. The experiments were carried out at 100°. The results indicate that neither *o*-carboxycinnamic, *o*-carboxyphenylglyceric, phthalylacetic, homophthalic, nor phthalidecarbonic acid can be formed as essential intermediate products in the oxidation of β-naphthaquinone, for the last-mentioned substance is more rapidly attacked than any of the preceding acids. Phthalonic acid is formed in the oxidation of all the acids mentioned, as well as by the oxidation of naphthaquinone. It is also considered that homophthalic acid cannot be an intermediate product in the oxidation of either *o*-carboxycinnamic, *o*-carboxyphenylglyceric, or phthalylacetic acid to phthalonic acid. From similar comparative experiments with α-naphthaquinone and α-naphthol, the author further considers that neither homophthalic, *o*-carboxycinnamic, nor phthalylacetic acid is an intermediate stage in the oxidation of α-naphthaquinone, and that homophthalic acid is not formed when α-naphthol is the original substance acted on.

Experiments made to ascertain the course of the oxidation of naphthalene by nitric acid permit of no definite conclusions on account of the formation of very considerable quantities of nitrated products. The yields of phthalic acid obtained in six hours at 100° with nitric acid of D 1·15 from naphthalene, α- and β-naphthaquinones, homophthalic, and phthalidecarboxylic acids are compared. H. M. D.

o-Nitroaniline. FRIEDRICH LEUCHS (*Ber.*, 1907, **40**, 1083—1087). —The author has prepared *o*-nitrosoacetanilide by a different method from that of Brand and Stohr (this vol., i, 100) with the object of studying the action of potassium cyanide and metallic salts on it (compare Piloty and Schwerin, Abstr., 1901, i, 516).

A 50% yield of the monoacetylphenylenediamine was obtained by the reduction of *o*-nitroacetanilide with tin foil and hydrochloric acid between 5° and 10°. The tin is best removed from the tin double salt by electrolysis. The m. p. is 132° (Manuelli and Galloni, Abstr., 1901, i, 413, give 145°). By oxidation with Caro's acid, the acetyl-*o*-phenylenediamine is converted into nitrosoacetanilide, yield 75—80%; this with potassium cyanide yields a substance crystallising in white, prismatic needles, m. p. 224°. W. R.

[Acetyl Derivatives of the Highly Chlorinated Alkylanilines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 176474).—The following acyl compounds combine with nitrocellulose to furnish products of the celluloid type, which are, however, much less inflammable than the material obtained from nitrocellulose and camphor. 2 : 4 : 6-*Trichloroacetomethylanilide*, m. p. 89—90°; 2 : 3 : 4 : 6-*tetrachloroacetomethylanilide*, m. p. 94—97°; *pentachloroacetomethylanilide*, m. p. 136—137°; 2 : 4 : 6-*trichloroacetoethylanilide*, m. p. 50—51°; 2 : 3 : 4 : 6-*tetrachloroacetoethylanilide*, m. p. 73—74°; 2 : 3 : 5 : 6-*tetrachloroacetoethylanilide*, m. p. 84—85°; *pentachloroacetomethylanilide*, m. p. 99—100°; 2 : 4 : 6-*trichloroacetobenzylanilide*, m. p. 61°; 2 : 3 : 4 : 6-*tetrachloroacetobenzylanilide*, m. p. 80—81°; 2 : 3 : 5 : 6-*tetrachloroacetobenzylanilide*, m. p. 97°.

Owing to their high melting points and sparing solubility the two following compounds are not suitable for the production of celluloid:

2 : 3 : 5 : 6-*Tetrachloroacetomethylanilide*, m. p. 175°; *pentachloroacetobenzylanilide*, m. p. 140°.

Pentachloroaniline, m. p. 245—246°, and the other chlorinated primary bases also yield acetyl derivatives which are too insoluble to be of use in this connexion. G. T. M.

Anilide of *iso*Succinic Acid. EZIO COMANDUCCI (*Rend. Accad. Sci. Fis. Nat. Napoli*, 1906, [iii], 12, 463—465. Compare Comanducci and Lobello, Abstr., 1905, i, 271).—The author confirms the results previously obtained (*loc. cit.*) concerning the formation of *iso*succinoanilide and *iso*succinodianilide by the action of aniline on ethyl *iso*succinate. The statement made by Meyer and Bock (Abstr., 1906, i, 726) that the dianilide is the only product of this reaction is hence inaccurate; the analytical results given by these authors are also erroneous, the proportions of carbon and hydrogen obtained corresponding with those for the monoanilide, whilst the percentage of nitrogen is equal to the calculated value for the dianilide. T. H. P.

β-*o*-Tolylethylamine. E. BLUMENFELD (*Bull. Acad. Sci., Cracow*, 1906, 274—276).—*β-o-Tolylethylamine*, formed together with *o*-xylene and *o*-tolylacetic acid by reduction of *o*-xylyl cyanide with sodium and alcohol, is obtained as a colourless oil, b. p. 215·5—217°, D^{18} 0·9615, n_D 1·527; the *hydrochloride*, m. p. 227—228°, *platinichloride*, and *hydrogen sulphate* were analysed. The *acetyl* derivative crystallises in white needles, m. p. 53°; the s-*thiocarbamide*,

$$CS(NH\cdot CH_2\cdot CH_2\cdot C_6H_4Me)_2,$$

m. p. 113·5°, crystallises from alcohol. G. Y.

Derivatives of *p*-Xylyl Cyanide. K. CIESIELSKI (*Bull. Acad Sci., Cracow*, 1906, 270—274. Compare Radziszewski and Wispek, Abstr., 1885, 889).—Two *by-products*, b. p. 250—260° and 260—270°, soluble in ether, are obtained in the preparation of *p*-xylyl cyanide from *p*-xylyl bromide and potassium cyanide.

p-*Tolylthioacetamide*, $C_6H_4Me\cdot CH_2\cdot CS\cdot NH_2$, formed by the action of hydrogen sulphide on the cyanide in alcoholic-ammoniacal solution, separates in colourless crystals, m. p. 113—114°.

β-p-*Tolylethylamine*, $C_6H_4Me\cdot CH_2\cdot CH_2\cdot NH_2$, prepared by reduction of the cyanide with sodium and alcohol, is obtained as an oil, b. p. 214·5°, D^{14} 0·9342, n_D^{18} 1·5240; the *hydrochloride*, $C_9H_{14}NCl$, glistening leaflets, m. p. 216—217°; the *platinichloride*,

$$(C_9H_{13}N)_2,H_2PtCl_6,$$

small, yellow leaflets decomposing at 230°; the *hydrogen sulphate*,

$$C_9H_{13}N,H_2SO_4,$$

needles or leaflets.

The action of nitrous acid on the amide leads to the formation of two *alcohols*, of which one, b. p. 217—218°, D^{22} 0·9972, $n_D^{22·5}$ 1·5253, gives the reactions of a secondary alcohol, whilst the other, b. p. 220—221°, D^{22} 0·99928, $n_D^{22·5}$ 1·5232, gives with potassium nitrite, potassium hydroxide, water, and sulphuric acid the red coloration characteristic of a primary alcohol. G. Y.

Asymmetric Nitrogen. XXVII. Asymmetric Ammonium Salts of the *p*-Phenetidine Series and the Resolution of *p*-Ethoxyphenylbenzylmethylallylammonium into its Optical Isomerides. EDGAR WEDEKIND and EMANUEL FRÖHLICH (*Ber.*, 1907, 40, 1001—1009. Compare Abstr., 1906, i, 162).—Quaternary ammonium bromides and iodides of the *p*-phenetidine series have been prepared each by three methods: by the action of the benzyl haloid on methylallyl-*p*-phenetidine; of the allyl haloid on benzylmethyl-*p*-phenetidine, and of the methyl haloid on benzylallyl-*p*-phenetidine. The results obtained differ from those in the *o*-anisidine series (*loc. cit.*) in that the three reactions yield identical products.

Methylallyl-p-*phenetidine*, prepared from methyl-*p*-phenetidine, b. p. 164°/40 mm., and allyl iodide, is a yellow oil, b. p. 191°/95 mm.

Benzylmethyl-p-*phenetidine*, prepared from methyl-*p*-phenetidine and benzyl bromide, is a viscid oil, b. p. 215—217°/25 mm.

Benzylallyl-p-*phenetidine*, prepared from benzyl-*p*-phenetidine, m. p. 45—46°, and allyl iodide, is a viscid, yellow oil, b. p. 238—240°/35 mm. The *picrate*, $C_{24}H_{24}O_8N_4$, forms yellow leaflets, m. p. 141°.

p-*Ethoxyphenylbenzylmethylallylammonium iodide* forms microscopic prisms, m. p. 128°. The *bromide* crystallises in microscopic, tetragonal plates, m. p. 139—140°. l-p-*Ethoxyphenylbenzylmethylallylammonium* d-*camphorsulphonate*, formed by the action of the inactive iodide or bromide on silver *d*-camphorsulphonate, crystallises in small prisms, m. p. 164°, $[\alpha]_D + 7{\cdot}95°$, $[M]_D + 40{\cdot}66°$, equivalent to $[M]_D - 11{\cdot}1°$ for the *p*-ethoxyphenylbenzylmethylallylammonium cation. The *iodide* of the *l*-base crystallises from a mixture of alcohol and ether, $[\alpha]_D - 1{\cdot}63°$, $[M]_D - 6{\cdot}65°$, in chloroform solution. The d-*bromocamphorsulphonate*, m. p. 146°, $[\alpha]_D + 45{\cdot}86°$; $[M]_D + 271°$; this salt could not be resolved by fractional crystallisation.

o-*Methoxyphenylbenzylmethylallylammonium bromide*, prepared from methylallyl-*o*-anisidine and benzyl bromide or from methylbenzyl-*o*-anisidine and allyl bromide, crystallises in hexagonal prisms, m. p. 106—107°. This base could not be resolved by fractional crystallisation of its d-*camphorsulphonate*, m. p. 108—109°, $[\alpha]_D + 10{\cdot}32$, $[M]_D + 51{\cdot}50°$. G. Y.

Asymmetric Nitrogen. XXVIII. Asymmetric Ammonium Salts of *p*-Anisidine. EMIL FRÖHLICH and EDGAR WEDEKIND (*Ber.*, 1907, **40**, 1009—1013. Compare preceding abstract).—The resolution of *p*-anisylbenzylmethylallylammonium bases into optically active components is rendered difficult on account of the sparing solubility of the *d*-bromocamphorsulphonates and the *d*-camphorsulphonates. The active cation, $\cdot NMe(C_3H_5)(C_7H_7)\cdot C_6H_4\cdot OMe(p)$, has $[M]_D + 17{\cdot}45°$.

Formyl-p-*anisidine*, $C_8H_9O_2N$, obtained by boiling a mixture of *p*-anisidine and 90% formic acid for two hours, separates from alcohol in prisms, m. p. 80—81°. Its alcoholic solution was acted on by sodium ethoxide and methyl iodide and the product then boiled with concentrated hydrochloric acid; the base obtained after the addition of sodium hydroxide was dissolved in dilute hydrochloric acid, converted by nitrous acid into a solid nitroso-compound, which on reduction and subsequent acidification yielded *methyl*-p-*anisidine*, $C_8H_{11}ON$, separating from light petroleum in microscopic crystals, m. p. 37°, b. p. 135—136°/19 mm.

Benzyl-p-*anisidine*, $C_{14}H_{15}ON$, obtained from *p*-anisidine (2 mol.)

and benzyl chloride (1 mol.), has b. p. 236—238°/32 mm., and separates from light petroleum in leaflets, m. p. 52°.

Methylallyl-p-*anisidine*, $C_{11}H_{15}ON$, obtained from methyl-*p*-anisidine and allyl iodide, is an oil, b. p. 172—173°/60 mm.

Benzylmethyl-p-*anisidine*, $C_{15}H_{17}ON$, obtained from methyl-*p*-anisidine and benzyl bromide, is a yellow oil, b. p. 220—222°/30 mm.

p-*Methoxyphenylbenzylmethylallyl ammonium iodide*, $C_{18}H_{22}ONI$, obtained either by the addition of benzyl iodide to methylallyl-*p*-anisidine or by the addition of allyl iodide to benzylmethyl-*p*-anisidine, separates from alcohol in prisms, m. p. 132—133°. The corresponding *bromide*, obtained by analogous methods, separates from alcohol in prisms, m. p. 147—148°.

A partial resolution of the base into its optically active components was accomplished by means of *d*-bromocamphorsulphonic acid, the fractionation of the camphorsulphonates having been conducted from a mixture of chloroform and ether. The most sparingly soluble fraction obtained gave a feebly active iodide with $a_D - 0{\cdot}05°$ ($c = 0{\cdot}776$, $l = 2{\cdot}5$) in chloroform solution. A better result was obtained by the use of *d*-camphorsulphonic acid, the iodide obtained in this case from the most sparingly soluble fraction having $[a]_D + 6{\cdot}39°$ in chloroform solution. The tendency of this chloroform solution to autoracemise was slight. A. McK.

Hydroanethole. J. TH. HENRARD (*Chem. Zentr.*, 1907, i, 343; from *Chem. Weekblad*, 3, 761—764).—When anethole and chavicol methyl ether are reduced with nickel and hydrogen, p-*propylanisole*, b. p. 213·5—214·5°/761 mm., is readily obtained in theoretical quantity. By the action of nitric acid on the product, a *nitro*-compound which crystallises in small yellow needles is formed. The *sulphonic acid*, $OMe{\cdot}C_6H_3Pr{\cdot}SO_3H,H_2O$, m. p. 94°, is readily soluble in water or alcohol, and soluble in warm benzene, toluene, or chloroform, but insoluble in cold ether. E. W. W.

Dibromides of Aromatic Propenyl Compounds. VI. Tribromo-*iso*safrole Dibromide. PAUL HOERING (*Ber.*, 1907, 40, 1096—1110. Compare Abstr., 1905, i, 902, 903, 592; 1904, i, 577).—Anethole and *iso*safrole are similar in most of their properties, but anethole with bromine gives a tetrabromide, whereas *iso*safrole yields a pentabromo-derivative, the constitution and properties of which are now described. *iso*Safrole and bromine interact, giving rise to a tetra- or penta-bromide according to the conditions; the pentabromide is formed when the *iso*safrole is dropped into excess of bromine, the temperature being kept at 32—35°; on the other hand, the tetrabromide is obtained free from pentabromide if the *iso*safrole is added quickly. *Tribromo*iso*safrole aβ-dibromide*, $CH_2O_2{:}C_6Br_3{\cdot}CHBr{\cdot}CHMeBr$, crystallises from a mixture of alcohol and benzene in small aggregates, m. p. 196·5—197°. It is stable towards aqueous acetone, hydrogen bromide, and alcoholic or molten potassium hydroxide. By oxidising agents, such as chromic acid and potassium permanganate, it is only slightly attacked, but it is easily reduced by zinc dust in a mixture of alcohol and benzene to *tribromo*iso*safrole*, $CH_2O_2{:}C_6Br_3{\cdot}CH{:}CHMe$, m. p.

110—111°. Excess of zinc has little action on the latter, but if the heating is continued for ten hours it yields a *dibromo*-derivative, $C_{10}H_8O_2Br_2$, m. p. 98·5—100°, and a small amount of a substance, m. p. 147—150°. Reduction with hydriodic acid, D 1·7, however, gives *tribromodihydro*iso*safrole*, $CH_2O_2{:}C_6Br_3{\cdot}CH_2{\cdot}CH_2Me$, crystallising from light petroleum in needles, m. p. 72—74°, insoluble in alkali. Tribromo*iso*safrole is thus shown to contain an ethylenic linking, which is also proved by its re-forming the original pentabromide when placed with bromine in sunlight; in diffused light, however, a new stereoisomeric *iso*safrole pentabromide is formed.

*iso*Safrole tetrabromide on reduction with zinc dust yields *dibromo*iso*safrole*, $C_{10}H_8O_2Br_2$, crystallising in needles, m. p. 149—150°, and, under similar conditions, bromo*iso*safrole dibromide yields *bromo*iso*safrole*, m. p. 30—33°, b. p. 165—170°/16 mm.

Tribromo*iso*safrole, when heated under pressure for five to six hours at 145—150° with alcoholic potassium hydroxide, yields the *ethoxymethyl ether* of *tribromopropylenecatechol*,

$$OEt{\cdot}CH_2{\cdot}O{\cdot}C_6Br_3(OH){\cdot}CH{:}CHMe,$$

m. p. 96—99°, which is easily hydrolysed by acid to *tribromopropylenecatechol*, $C_6Br_3(OH)_2{\cdot}C_3H_5$, m. p. 111—113°. The *dimethyl ether*, $C_{11}H_{11}O_2Br_3$, has m. p. 98—99·5°; the *methyl ethoxymethyl ether*, $OEt{\cdot}CH_2{\cdot}O{\cdot}C_6Br_3(OMe){\cdot}C_3H_5$, m. p. 78—80°; the *methyl ether*,

$$C_{10}H_9O_2Br_3,$$

m. p. 135—137°, and the *diacetate*, $C_{13}H_{11}O_4Br_3$, m. p. 128—130°.

Tribromo-*iso*safrole dibromide, when heated with silver acetate, gives 4 : 5 : 6-*β-tetrabromo-α-acetoxydihydro*iso*safrole*,

$$CH_2O_2{:}C_6Br_3{\cdot}CH(OAc){\cdot}CHBr{\cdot}CH_3,$$

m. p. 178—180°; the reaction is not complete when sodium acetate is used. *Tribromo*iso*safrole oxide*, $CH_2O_2{:}C_6Br_3{\cdot}CH{<}\overset{CHMe}{\underset{O}{|}}$, obtained when the above acetoxy-compound is heated with alcoholic potassium hydroxide, has m. p. 201—202°, forms an additive compound with acetyl bromide, 2 : 4 : 6-*α-tetrabromo-β-acetoxydihydro*iso*safrole*,

$$CH_2O_2{:}C_6Br_3{\cdot}CHBr{\cdot}CHMe{\cdot}OAc,$$

m. p. 179—181°; a melting point determination of the mixture of the α-bromo- and β-bromo-derivatives gives 150—155°. *Tribromo-α-hydroxy-β-acetoxydihydro*iso*safrole*, $C_{12}H_{11}O_5Br_3$, m. p. 174—175°, is obtained by heating the α-bromo-β-acetoxy-compound in toluene with excess of silver nitrate, and on hydrolysis with alcoholic potassium hydroxide yields *tribromo*iso*safrole glycol*, $CH_2O_2{:}C_6Br_3{\cdot}CH(OH){\cdot}CHMe{\cdot}OH$, of m. p. 159—161°, sintering at 110°. The *diacetate*, $C_{14}H_{13}O_6Br_3$, has m. p. 154—156°. On oxidising this glycol with potassium permanganate on the water-bath, *tribromopiperonal*, $CH_2O_2{:}C_6Br_3{\cdot}CHO$, crystallising in needles, m. p. 197—201°, is obtained. The *semicarbazone*, $C_9H_6O_3N_3Br_3$, does not melt at 240°. *Tribromopiperonylic acid*, $C_8H_3O_4Br_3$, from the corresponding aldehyde, is a crystalline powder, m. p. 233°.

Tribromopropylenecatechol dibromide, $C_6Br_3(OH)_2{\cdot}CHBr{\cdot}CHMeBr$, is obtained from tribromopropylenecatechol and bromine in sunlight, m. p. 85—90°.

W. R.

Action of Phenols on Trichloroacetic Acid. OTTO ANSELMINO (*Chem. Zentr.*, 1907, i, 339; from *Ber. deut. Pharm. Ges.*, 16, 390—393).—Lossen and Eichloff have found that when trichloroacetic acid is heated with water or with 1 mol. of alkali hydroxide, chloroform and carbon dioxide are formed, whilst by the action of 6 mols. of hydroxide, formic acid and carbon dioxide are obtained, and with less than 6 mols. of hydroxide, both reactions occur. The fact that in the reaction given by the German Pharmacopœia IV the odour of chloroform is not always produced, is to be ascribed therefore to the use of too great an excess of alkali. Chloroform and carbon dioxide are also obtained when trichloroacetic acid is heated with resorcinol or cresol, but the decomposition is much slower in the latter case. By the action of phenol or thymol, trichloroacetic acid forms hydrogen chloride, carbon oxychloride, and carbon monoxide; hence the alleged formation of the so-called *Thymylum trichloraceticum* (*Pharm. Centr.-h.*, 46, 684) by heating trichloroacetic acid with thymol is incorrect. *Thymol trichloroacetate*, $C_{12}H_{13}O_2Cl_3$, b. p. 110—111°/12 mm., which can only be prepared by the action of sodium-thymol on trichloroacetyl chloride, forms a clear liquid, but gradually becomes bluish-green on exposure to air; it is insoluble in alkalis, and is readily hydrolysed, but cannot be distilled under the ordinary pressure without decomposition.
E. W. W.

Condensation of Resorcinol. RICHARD MEYER and KARL MARX (*Ber.*, 1907, 40, 1450—1453).—When resorcinol is heated, alone at 200—220° or with zinc chloride at 160—180°, a brown, fluorescent condensation product is obtained, from which a small quantity of a *substance*, $C_{14}H_{12}O_3$, m. p. 263°, can be isolated; this crystallises in slender, colourless needles, and dissolves in alkalis without fluorescence; the *acetate*, $C_{14}H_{10}O(OAc)_2$, has m. p. 150—151°, and the *benzoate*, $C_{14}H_{10}O(OBz)_2$, m. p. 180° (compare Grimaux, Abstr., 1895, i, 655).
C. S.

Condensation of Aromatic Hydrocarbons with the Carbohydrates, Cellulose, and Dextrose. ALEXANDER M. NASTUKOFF (*Zeitsch. Farb. Ind.*, 1907, 6, 70—71. Compare Abstr., 1902, i, 362 and 747).—The method of treating cellulose with benzene in presence of sulphuric acid, formerly described, has been slightly modified, the product obtained under the new conditions containing only a small proportion (0·43%) of sulphur; the substance obtained, termed *β-phenyldesoxyn* to distinguish it from the former material to which the name of *a-phenyldesoxyn* is given, appears to have the composition $C_6H_7O_2Ph_3$, derived from cellulose by the replacement of three hydroxyl by three phenyl groups. The homologues of benzene (toluene, xylene, ψ-cumene) give *desoxyns* with cellulose similar to that obtained with benzene. The oxidation of β-phenyldesoxyn by permanganate gives 45% of benzoic acid, that of *tolyldesoxyn* giving 20% of terephthalic acid; *xylyldesoxyn*, prepared from commercial xylene, gives 4% of terephthalic acid and 25% of trimellitic acid; *ψ-cumyldesoxyn* gives pyromellitic acid. In all these cases carbonic acid and oxalic acid (about 15%) are also formed. The cellulose residue appears in all cases to enter the benzene nucleus in the para position relative to methyl.

Dextrose, like cellulose, also combines with benzene, forming apparently a compound in which three hydroxyl groups have been replaced by three phenyl radicles. W. A. D.

Action of *pp*-Tetramethyldiaminobenzhydrol on Certain Methylenic Compounds.

Robert Fosse (*Compt. rend.*, 1907, **144**, 643—644).—*pp*-Tetramethyldiaminobenzhydrol condenses with *β*-ketonic esters and diketones, with elimination of H_2O, and formation of a new class of compounds of which the constitution is at present undetermined. *Ethyl* pp-*tetramethyldiaminobenzhydrylacetylacetate*, $C_{23}H_{30}O_3N_2$, m. p. 128—129°, dissolves in cold acetic acid to a colourless solution which becomes blue on heating, and the coloration persists on cooling. Its *dimethiodide*, $C_{25}H_{36}O_3N_2I_2$, m. p. 180—181°, forms small, greyish-yellow crystals which become green in the capillary tube at 175°; the acetic acid solution is colourless both when hot and cold. The acetate forms a *dihydrochloride*, $C_{23}H_{30}O_3N_2,2HCl$ and a *platinichloride*,

$$C_{23}H_{30}O_3N_2,H_2PtCl_6.$$

Ethyl pp-*tetramethyldiaminobenzhydrylbenzoylacetate*, $C_{28}H_{32}O_3N_2$, m. p. 181—182°, dissolves in cold acetic acid to a colourless solution which becomes blue on heating; it forms a *platinichloride*,

$$C_{28}H_{32}O_3N_2,H_2PtCl_6.$$

pp-*Tetramethyldiaminobenzhydrylacetylacetone*, $C_{22}H_{28}O_2N_2$, m. p. 148—149°, and pp-*tetramethyldiaminobenzhydrylbenzoylacetone*,

$$C_{27}H_{30}O_2N_2,$$

m. p. 160°, both give acetic acid solutions behaving as with the above bases. *Ethyl* pp-*tetramethyldiaminobenzhydrylmalonate*, $C_{24}H_{32}O_4N_2$, forms long, silky needles, m. p. 128—130°, which give a *platinichloride*, $C_{24}H_{32}O_4N_2,H_2PtCl_6$; the *acid*, $C_{18}H_{22}N_2(CO_2H)_2$, is obtained by saponifying the ester with potash and treating the solution obtained with sulphuric acid; when boiled with 30% sulphuric acid it is converted into *pp*-tetramethyldiaminodiphenyl-*ββ*-propionic acid,

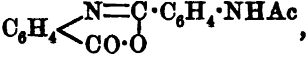
$$CH(C_6H_4\cdot NMe_2)_2\cdot CH_2\cdot CO_2H,$$

already described (Abstr., 1906, i, 975). *pp*-Tetramethyldiaminobenzhydrylmalonic acid has not a definite melting point, but when thrown on to a mercury-bath at 200—205° it turns a light green, melts, intumesces, and solidifies to a rust-coloured substance, m. p. 225—230°; if kept for ten minutes at 188° it becomes light green, then, without melting, rust-coloured with m. p. 225°. The *potassium* salt,

$$C_{18}H_{22}N_2(CO_2K)_2,$$

forms small, brilliant needles, and the *sodium* salt forms brilliant, silvery scales, both containing alcohol of crystallisation; the hydrated *barium* salt forms colourless spangles; the hydrated *calcium* salt small, silvery crystals, and the *lead* salt a white precipitate. The acid and its alkali salts form colourless acetic acid solutions which become blue on heating, and in the case of the potassium salt even on keeping in the dark. E. H.

Acetylation of Anthranoylanthranilic [*o*-Aminobenzoylanthranilic] Acid.

Ernst Mohr and Friedrich Köhler (*Ber.*, 1907, **40**, 997—999. Compare Abstr., 1906, i, 359; Anschütz, Schmidt, and Greiffenberg, Abstr., 1903 i, 57).—The action of an excess of acetic anhydride on *o*-aminobenzoylanthranilic acid leads to the formation of the *lactimone*,  $C_6H_4<\begin{matrix}N{=}C\cdot C_6H_4\cdot NHAc\\ CO\cdot O\end{matrix}$, so termed because containing the lactime, $\cdot O\cdot C\colon N\cdot$, as also the lactone group $\cdot C\cdot CO\cdot O\cdot C\cdot$. It separates from benzene in white crystals, m. p. 211°, is insoluble in cold aqueous ammonia, and is an analogue of the anhydride of *o*-acetoxybenzoylanthranilic acid (Meyer, this vol., i, 317) and of the acylanthranils. When heated with alcoholic ammonia, the lactimone yields *o-acetylaminobenzoylanthranilamide*,

$$NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2,$$

which crystallises in thin, white prisms, m. p. 226°, evolving gas.

G. Y.

Spacial Isomerism in the Phenylnitrocinnamic Acids (Anhydrides, Indones, Chlorides, Phenylhydrazides, Hydrazones, and Oximes).—MARUSSIA BAKUNIN and L. PARLATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 503—515. Compare Abstr., 1895, i, 531; 1897, i, 622, and 1906, i, 664).—The authors have investigated various derivatives of the stereoisomeric forms of phenyl-*m*- and *p*-nitrocinnamic acids. Of each of the two pairs of stereoisomerides, one (the allo-isomeride) forms a salt with phenylhydrazine more readily than the other, which, in its turn, is more easily converted into an acid-chloride by reaction with phosphorus pentachloride in a neutral solvent. With phenylhydrazine, the anhydrides of the acids behave like anhydrides of other monobasic acids, giving rise to phenylhydrazides. The two *m*-acids yield the same indone, as also do the two *p*-acids; the presence of the carbonyl group in the indones is shown by the products they give with phenylhydrazine and hydroxylamine. The esters of these acids are best prepared by boiling the acids with phosphoric oxide in a neutral solvent and boiling the crude anhydrides so obtained with the corresponding alcohols.

In the preparation of phenyl-*m*- and *p*-nitrocinnamic acids by Perkin's synthesis, these acids are accompanied by *m*-nitrobenzylidene diacetate, m. p. 72°, and *p*-nitrobenzylidene diacetate, m. p. 127°, both of which are insoluble in sodium carbonate solution.

Phenyl-*m*-nitrocinnamic acid is obtained in two isomeric forms: (1) the *allo*-isomeride, m. p. 195°; the *phenylhydrazine* salt, $C_{15}H_{11}O_4N,NHPh\cdot NH_2$, separates in yellowish-white, silky plates, m. p. 142°; the corresponding *phenyl*-m-*nitrocinnamoyl chloride*, $C_{15}H_{10}O_3NCl$, is deposited from benzene in granules or glassy crystals, m. p. 89—90°; the *anhydride*, $(C_{15}H_{10}O_3N)_2O$, has m. p. 139°. (2) The *ordinary* form, m. p. 181°; the *phenylhydrazine* salt, $C_{15}H_{11}O_4N,NHPh\cdot NH_2$, crystallises from benzene or alcohol in silky needles, m. p. 118—120°; the corresponding *phenyl*-m-*nitrocinnamoyl chloride*, $C_{15}H_{10}O_3NCl$, crystallises from benzene in shining, glassy prisms, m. p. 90—92°; the *anhydride* has m. p. 151°.

Phenyl-*p*-nitrocinnamic acid also occurs in two forms: (1) the *allo*-isomeride, m. p. 147° or, in the hydrated condition, 105°; the *phenylhydrazine* salt, $C_{15}H_{11}O_4N,NHPh\cdot NH_2$, separates in canary-yellow needles, m. p. 172°; the corresponding *phenyl*-p-*nitrocinnamoyl chloride*,

$C_{15}H_{10}O_3NCl$, crystallises in slender, straw-yellow needles, m. p. 90—91°; the *anhydride* has m. p. 182°. (2) The *ordinary* form, m. p. 214°; the corresponding *phenylhydrazine* salt crystallises from alcohol in tufts of slender, golden-yellow needles, m. p. 136—137°; the corresponding *phenyl*-p-*nitrocinnamoyl chloride* crystallises from light petroleum in straw-yellow needles, m. p. 95—97°; the *anhydride* has m. p. 162°.

Phenyl-p-*nitroindone*, $C_{15}H_9O_3N$, crystallises in monoclinic, rhomboidal plates, m. p. 217°; its *phenylhydrazone*, $C_{15}H_9O_2N\colon N\cdot NHPh$, separates from alcohol as a vermilion-red powder, m. p. 196°; the *oxime*, $C_{15}H_9O_2N\colon N\cdot OH$, crystallises from alcohol or benzene in orange-yellow needles, m. p. 235°.

Phenyl-m-*nitroindone* has m. p. 218°; its *phenylhydrazone* crystallises from alcohol or benzene in blood-red clots, m. p. 182·5°; the *oxime* crystallises from alcohol or benzene in cadmium-yellow needles, m. p. 246°.

Ordinary *phenyl*-p-*nitrocinnamoyl phenylhydrazide*,

$$C_{15}H_{10}O_3N\cdot NH\cdot NHPh,$$

prepared by the action of phenylhydrazine on the anhydride or chloride of the corresponding acid, crystallises from alcohol or benzene in flocks of straw-yellow needles, m. p. 141°.

allo*Phenyl*-p-*nitrocinnamoyl phenylhydrazide*, prepared similarly to the preceding compound, crystallises from alcohol in plates composed of straw-yellow needles, m. p. 220—221°.

Ordinary *phenyl*-m-*nitrocinnamoyl phenylhydrazide* separates from alcohol in small, rhombohedral crystals, m. p. 143°, or from benzene in long, silky needles, m. p. 80°, which, after losing their benzene of crystallisation and resolidifying, have m. p. 143°.

allo*Phenyl*-m-*nitrocinnamoylphenylhydrazide* crystallises from alcohol or benzene in flocks of white needles, m. p. 186—187°.

All these phenylhydrazides are moderately stable and are insoluble in sodium carbonate solution.

Methyl phenyl-m-*nitrocinnamate*, $C_{15}H_{10}O_4NMe$, crystallises in long, straw-yellow, monoclinic prisms, m. p. 83—84°; the corresponding *ethyl* ester crystallises from alcohol in tufts of elongated prisms, or from light petroleum in elongated, monoclinic prisms with an irregular, polygonal section, m. p. 80°.

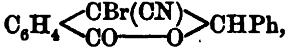
Methyl phenyl-p-*nitrocinnamate* crystallises from alcohol in monoclinic needles, m. p. 141°, and the corresponding *ethyl* ester is deposited from alcohol in tufts of needles, or from light petroleum in short, apparently monoclinic prisms, m. p. 100—102°.

Methyl phenyl-o-*nitrocinnamate* has m. p. 75—76°. T. H. P.

Condensation of Benzylcyanide-*o*-carboxylic Acid with Aldehydes. JOSEPH GYR (*Ber.*, 1907, 40, 1201—1214. Compare Bistrzycki and Stelling, Abstr., 1901, i, 718).—*a-Cyanostilbene*-2-*carboxylic acid*, $CHPh\colon C(CN)\cdot C_6H_4\cdot CO_2H$, m. p. 163° (decomp.), resulting from the condensation of equal molecular quantities of benzyl-cyanide-*o*-carboxylic acid and benzaldehyde in the presence of 30% sodium hydroxide, forms white prisms or needles; the *silver* salt,

$C_{16}H_{10}O_2NAg$, is fairly stable to light; the *ethyl* ester, m. p. 62·5°, crystallises in well-defined, monoclinic needles, $[a:b:c = 1·6066:1:2·3310]$.

4-*Bromo-4-cyano-3-phenyldihydroisocoumarin*,



$$C_6H_4<\substack{CBr(CN)\\ CO\text{——}O}>CHPh,$$

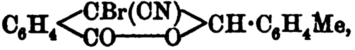
m. p. 165° (decomp.), is obtained by the action of bromine on the preceding ester dissolved in chloroform or by treating the acid with bromine in 50% sodium carbonate solution and acidifying the mixture with dilute sulphuric acid. The lactone crystallises in white needles, is decomposed by warm $N/1$ potassium hydroxide, yielding benzaldehyde, and is converted at its melting point into Gabriel and Neumann's 4-cyano-3-phenyl*iso*coumarin (Abstr., 1893, i, 228).

a-Cyano-4'-methylstilbene-2-carboxylic acid,

$$C_6H_4Me·CH:C(CN)·C_6H_4·CO_2H,$$

m. p. 151°, derived from *p*-tolualdehyde, forms white needles; the *silver* and *sodium* salts are mentioned. Heated at 20° above its m. p., the acid changes into the isomeric *lactone*, m. p. 157°, the constitution of which is not settled.

4-*Bromo-4-cyano*-3-p-*tolyldihydro*iso*coumarin*,



$$C_6H_4<\substack{CBr(CN)\\ CO\text{——}O}>CH·C_6H_4Me,$$

m. p. 173° (decomp.), obtained from the preceding acid and bromine in chloroform or in sodium carbonate solution, crystallises in needles, and at its m. p. changes into Harper's 4-cyano-3-*p*-tolyl*iso*coumarin (Abstr., 1897, i, 106).

3'-*Hydroxy-a-cyanostilbene*-2-*carboxylic acid*,

$$OH·C_6H_4·CH:C(CN)·C_6H_4·CO_2H,$$

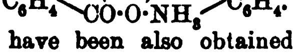
m. p. 159—161°, derived from *m*-hydroxybenzaldehyde, crystallises in needles and is soluble in sodium carbonate to a yellow solution.

2'-*Nitro-a-cyanostilbene*-2-*carboxylic acid*,

$$NO_2·C_6H_4·CH:C(CN)·C_6H_4·CO_2H,$$

m. p. 194°, derived from *o*-nitrobenzaldehyde in the presence of 30% sodium hydroxide, crystallises in needles; the *sodium* salt,

$$C_{16}H_9O_4N_2Na,3H_2O,$$

and the *barium* salt, $(C_{16}H_9O_4N_2)_2Ba,5H_2O$, form yellow needles. Reduction of the acid by alcoholic ammonium sulphide yields a *substance*, m. p. 245° (decomp.), which appears to be an internal salt of 2'-amino-a-cyanostilbene-2-carboxylic acid,  $C_6H_4<\substack{C(CN):CH\\ CO·O·NH_3}>C_6H_4$.

The following condensation products have been also obtained: 2'-*chloro-a-cyanostilbene-2-carboxylic acid*, m. p. 182°; 3'-*chloro-a-cyanostilbene-2-carboxylic acid*, m. p. 148°; 4'-*chloro-a-cyanostilbene*-2-*carboxylic acid*, m. p. 181—182°; *a-cyano-3'*:4'-*dimethoxystilbene*-2:2'-*dicarboxylic acid*, m. p. 194° (decomp.), derived from opianic acid.

iso*Nitrosobenzyl-cyanide*-o-*carboxylic acid*, $CO_2H·C_6H_4·C(CN):N·OH$, m. p. 235° (decomp.), is obtained as the sodium salt from benzylcyanide-*o*-carboxylic acid, amyl nitrite, and sodium ethoxide in alcoholic solution; it separates from dilute alcohol in greyish-white, microcrystalline needles. C. S.

Occurrence of Abietic Acid in Resin-Oil. Alexander Tschirch and Max Wolff (*Arch. Pharm.*, 1907, **245**, 1—4).—From a solution of resin-essence in ether, 5% aqueous sodium carbonate extracted about 30% of acids which, when crystallised first from a mixture of methyl and ethyl alcohols and then from acetic acid, yielded an abietic acid with m. p. 166—167°, composition $C_{19}H_{28}O_2$ or $C_{20}H_{30}O_2$, and acid number 194, corresponding with monobasicity. One % aqueous potassium hydroxide then extracted a small quantity of phenolic substances, and the bulk of the residue distilled between 315 and 385°. The yield of acid varies; it is greatest when the essence or oil has been obtained by distillation under diminished pressure.

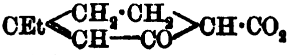
C. F. B.

Derivatives of Methyl*cyclo*hexane. Wladimir B. Markownikoff and V. Smirnoff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, i, 1—6. Compare Abstr., 1905, i, 760).—Methyl-3-*cyclo*hexanol was employed as a starting point for the preparation of methyl*cyclo*hexane-3-carboxylic acid. When treated with potassium cyanide the former yields a crystalline mass, which, when acted on by weak acids, forms an oily liquid yielding *crystals*, m. p. 63—64°, $a_D - 12°$, and corresponding with the formula $C_8H_{13}ON$. With hydrochloric acid, little of the corresponding hydroxy-acid is obtained, most of it being converted into crystalline condensation products free from nitrogen. With sulphuric acid, the cyanohydrin yields the corresponding *amide*, m. p. 120—121°, which, with dilute acid, forms *3-hydroxymethyl*cyclo*hexane-3-carboxylic acid*, $OH{\cdot}C_6H_9Me{\cdot}CO_2H$, b. p. 260—270°/723 mm. (slight decomp.). This acid must be a mixture of the *cis*- and *trans*-modifications, for when heated with aniline it yields two *anilides*, $C_{14}H_{19}ON_2$, m. p. 90—91°, $a_D - 17{\cdot}93°$, and m. p. 118·5—119·5°, $a_D - 13{\cdot}87°$. Both anilides yield the acid when treated with alkalis. A crystalline *sodium* salt of the acid has also been obtained, but it was found impossible to convert it to methyl*cyclo*hexane-3-carboxylic acid; with hydriodic acid and red phosphorus, it yields condensation products containing iodine, and carbon monoxide and dioxide.

Z. K.

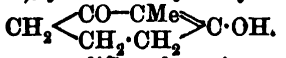
β-Chloroethyl Ketones and Alkyl Vinyl Ketones. Fixation of Sodio-derivatives. Edmond E. Blaise and M. Maire (*Compt. rend.*, 1907, **144**, 572—574. Compare Abstr., 1906, i, 142).—It has been shown (this vol., i, 241) that the alkyl vinyl ketones readily condense with organic sodium compounds, but, since these ketones readily polymerise in the presence of alkalis, the yields are small and the investigation has been extended to the β-chloroethyl ketones.

Ethyl β-chloroethyl ketone condenses with ethyl sodioacetoacetate to yield the *diketone*, $COMe{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}COEt$, which cannot be distilled without decomposing, even under a pressure of 4 mm., and gives a bluish-violet coloration with ferric chloride. On treatment with hydrogen chloride in presence of benzene it furnishes *3-ethyl-Δ²-*cyclo*hexenone-6-carboxylate*,



$CEt<\begin{matrix}CH_2{\cdot}CH_2\\ CH{-\!-}CO\end{matrix}>CH{\cdot}CO_2Et$, which on hydrolysis furnishes *3-ethyl-Δ²-*cyclo*hexenone*. In an analogous manner, with the sodium derivative of acetylacetone, ethyl-β-chloroethyl ketone yields the *triketone*, $CH(COMe)_2\cdot CH_2\cdot CH_2\cdot COEt$, which in the manner already indicated may be converted into 6-*acetyl*-3-*ethyl*-Δ^2-cyclo*hexenone*.

From the sodium derivative of ethyl malonate by the general reaction, the *ketonic* ester, $COEt\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$, is produced, and the dibasic acid corresponding with this decomposes when heated, yielding γ-propionylbutyric acid, which, by Vorländer's method (Abstr., 1896, i, 20; 1897, i, 272), yields methyl dihydroresorcinol,



$$CH_2<\begin{matrix}CO-CMe\\CH_2\cdot CH_2\end{matrix}>C\cdot OH.$$

The last-mentioned substance differs from its next lower homologue in being insoluble in ether, almost insoluble in water, and slightly soluble in cold alcohol, but the value of its molecular refraction indicates that, like the latter, it possesses the keto-enolic structure. T. A. H.

Salts of *cyclo*Gallipharic Acid. HERMANN KUNZ-KRAUSE and RUDOLF RICHTER (*Arch. Pharm.*, 1907, **245**, 28—42. Compare Abstr., 1904, i, 587).—The new salts prepared are enumerated below with their melting points; often the salts softened several degrees before they actually melted, and at the high temperature at which two of the lead salts melted, decomposition occurred ($A = C_{21}H_{35}O_8 = OH\cdot C_{20}H_{34}\cdot CO\cdot O\cdot$). Like the higher fatty acids, *cyclo*gallipharic acid dissolves readily when warmed with a concentrated solution of an alkali carbonate, but hardly at an appreciable rate in a dilute solution; moreover, the alkali *cyclo*gallipharates undergo hydrolysis when their aqueous solution is much diluted, the acid being precipitated. The salts, other than those of the alkali metals, were prepared by precipitation by means of a solution of the acid in the equivalent amount of normal potassium hydroxide solution. In the preparation of the ferric salt, no oxidation of the acid took place.

KA, 73·5°, crystalline. $BaA_2,2H_2O$, 121°; water not lost even at this temperature. CdA_2, 135·5°. CuA_2,H_2O, 81°; water lost at 100°, but not at the ordinary temperature under diminished pressure. $HgA_2,3H_2O$, 139·5°; water not lost at 100°. $4PbA_2,Pb(OH)_2$, 185—187°; $3PbA_2,Pb(OH)_2$, 225—230°; also a crystalline salt, m. p. 88°, containing 2·5% of lead, that is, one-tenth of the amount required by PbA_2. The basic salt, $OH\cdot FeA_3$, was the only ferric salt obtainable. C. F. B.

Hydrophthalic Acids. IV. $\Delta^{2:5}$-*cyclo*Hexadiene-1 : 2-dicarboxylic Acid. Constitution of the $\Delta^{2:5}$- and $\Delta^{1:3}$-Acids. GINO ABATI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], 12, 466—473. Compare Abstr., 1906, i, 959).—The author describes his further investigations on the anhydride obtained by heating $\Delta^{1:3}$-*cyclo*hexadiene-1 : 2-dicarboxylic anhydride for about two hours at 210—230° (*loc cit.*), and shows it to be the $\Delta^{2:5}$-anhydride.

$\Delta^{2:5}$-cyclo*Hexadiene*-1 : 2-*dicarboxylic anhydride*, $C_8H_6O_3$, crystallises from light petroleum in white, nacreous scales, m. p. 73—74°, and from benzene in shining prisms, m. p. 120°, containing $\frac{1}{2}C_6H_6$. For the corresponding acid, conductivity measurements give the values $\mu_\infty = 377$ and $K = 0\cdot0544$. After the anhydride has been boiled with

10% sodium hydroxide solution, it can be recovered unchanged by the addition of hydrochloric acid, so that $\Delta^{2:5}$-*cyclo*hexadiene-1 : 2-dicarboxylic acid does not exhibit the lability attributed to acids unsaturated in the βγ-position (*loc. cit.*, and Baeyer, Abstr., 1892, 1211). On reduction with sodium amalgam, the $\Delta^{2:5}$-acid is converted into Δ^{1}-*cyclo*hexene-1 : 2-dicarboxylic acid. Treatment of the $\Delta^{2:5}$-anhydride with bromine vapour, and subsequently with aqueous alcohol, converts it into the *dibromo-acid*, $C_6H_6Br_2(CO_2H)_2$, m. p. 197—198° (decomp.).

Support is lent to the $\Delta^{1:3}$- and $\Delta^{2:5}$-constitutions attributed to the dihydrophthalic acids described by the author (*loc. cit.*) by (1) the values of their affinity constants, and (2) the fact that the first, although it possesses two double linkings, does not form an additive compound with either bromine or hydrogen bromide, whilst the second combines with two atoms of bromine (compare Baeyer, *loc. cit.*).

T. H. P.

Hydrophthalic Acids; Reduction of Phthalic Acid by Means of Sodium Amalgam. V. GINO ABATI and SALVATORE MINERVA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1906, [iii], **12**, 473—498. Compare von Baeyer, Abstr., 1892, 1211; Abati and de Bernardinis, Abstr., 1905, i, 599).—The authors have reduced a large quantity of phthalic acid by means of sodium amalgam and have subjected the resultant mixture to a very thorough fractionation.

Besides the acids obtained by von Baeyer (*loc. cit.*) and the $\Delta^{1:3}$-*cyclo*hexadiene-1 : 2-dicarboxylic and *cis*-Δ^{3}-*cyclo*hexene-1 : 2-dicarboxylic anhydrides obtained by Abati and de Bernardinis (*loc. cit.*), the authors have isolated $\Delta^{1:4}$-*cyclo*hexadiene-1 : 2-dicarboxylic anhydride and have confirmed the formation of *cis*-$\Delta^{3:5}$-*cyclo*hexadiene-1 : 2-dicarboxylic acid. The $\Delta^{2:4}$- and $\Delta^{2:5}$-*cyclo*hexadiene-1 : 2-dicarboxylic, the Δ^{1}- and *cis*-Δ^{4}-*cyclo*hexene-1 : 2-dicarboxylic, and the two *cyclo*hexane-1 : 2-dicarboxylic acids could not be traced. The $\Delta^{2:4}$-dihydro-acid is reduced by sodium amalgam into the *cis*-Δ^{4}-tetrahydro-acid and this, when boiled with sodium hydroxide solution, is transformed into a mixture of the *trans*-Δ^{4}- and the Δ^{2}-tetrahydro-acids; the $\Delta^{2:5}$-dihydro-acid is converted by sodium amalgam into the Δ^{1}-tetrahydro-acid. The *cis*-and *trans*-*cyclo*hexane-1 : 2-dicarboxylic acids are formed with some degree of readiness only from the Δ^{1}-tetrahydro-acid. But the latter acid, although stable, is not found among the products of the reduction of phthalic acid by sodium amalgam, and it is this fact alone which prevents the conclusion that this reduction gives rise to all the hydrophthalic acids compatible with the conditions of experiment.

$\Delta^{1:4}$-cyclo*Hexadiene*-1 : 2-*dicarboxylic acid* has m. p. 153° and the corresponding *anhydride*, m. p. 134—135°.

cis-$\Delta^{3:5}$-cyclo*Hexadiene*-1 : 2-*dicarboxylic acid* has m. p. 174° (compare Abati and de Bernardinis, *loc. cit.*) and the corresponding *anhydride*, m. p. 100°.

T. H. P.

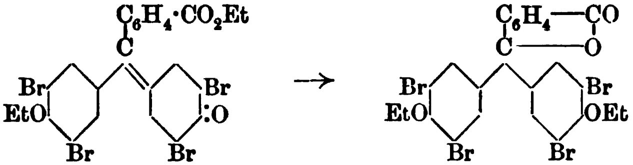
β-Methyl*cyclo*hexanyl Hydrogen Phthalate. V. TSCHECHOWITSCH (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, i, 6—8. Compare Abstr., 1904, i, 383).—*β-Methyl*cyclo*hexanyl hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_7H_{11}$, has been isolated as one of the intermediate products in the conversion of methyl*cyclo*hexane into heptanaphthene by means of phthalic anhydride. It forms prismatic crystals soluble in alcohol, ether, or benzene, m. p. 89·5—90·5°, $[\alpha]_D + 8·68—8·41°$.

Z. K.

Bromination of Santonin. JOSEPH KLEIN (*Ber.*, 1907, **40**, 939—942. Compare Klein, Abstr., 1893, i, 112; Wedekind and Koch, *ibid.*, 1905, i, 212).—Contrary to the statements of Wedekind and Koch, and in agreement with the author's earlier experiments, it is shown that the compound termed santonin acetate dibromide is obtained when bromine reacts with an acetic acid solution of santonin. It is essential, however, that the acetic acid should contain water (some 5%), as otherwise Wedekind and Koch's compound is formed. It has the composition $C_{15}H_{18}O_3Br_2$. When a small amount of santonin is dissolved in 1 c.c. of concentrated sulphuric acid, then mixed with an equal volume of water and a drop of ferric chloride solution, a characteristic violet coloration is obtained. Bromosantonin does not give this coloration unless previously boiled with sodium hydroxide solution. The dibromide gives a coloration which is somewhat more reddish-yellow in colour.

J. J. S.

Constitution of Phthalein Salts. RICHARD MEYER and KARL MARX (*Ber.*, 1907, **40**, 1437—1441. Compare Green and King, Abstr., 1906, i, 670).—The action of ethyl iodide on the dry silver salt of tetrabromophenolphthalein suspended in benzene gives Nietzki and Burckhardt's intensely yellow diethyl quinonoid derivative; m. p. 160—163° (Abstr., 1897, i, 225, m. p. given 150—151°); when recrystallised from carbon tetrachloride it gives sulphur-yellow needles, m. p. 63—65°, containing one molecule of carbon tetrachloride of crystallisation. This is the first time a quinonoid derivative of phenolphthalein has been obtained from a salt; the colourless diethoxy-lactoid derivative is obtained from the quinonoid compound either by solution in alcohol, light petroleum, or by fusion:



W. R.

Resoflavin and Galloflavin. JOSEF HERZIG and RUDOLF TSCHERNE (*Annalen*, 1907, **351**, 24—37. Compare Abstr., 1904, i, 814).—A study of the derivatives of resoflavin has established for this substance the formula $C_{14}H_8O_4(OH)_3$, and has shown that it must contain two anhydride groupings, and is a derivative of diphenylmethylolid (compare Graebe, Abstr., 1903, i, 262; Perkin and Nierenstein, Trans., 1904, **87**, 1412).

Methylresoflavin, m. p. 286—288° (282—283°. *loc. cit.*), dissolves in potassium hydroxide, and on acidification is deposited only slowly and on heating. When heated with methyl iodide and potassium hydroxide, it forms an *ether ester*, $C_{14}H_8O_2(OMe)_7$, separating in white crystals, m. p. 132—134°; on hydrolysis this yields the crystalline *ether acid*, $C_{14}H_4O_8(OMe)_6$, m. p. 197—199°, which when heated with hydriodic acid is converted into resoflavin.

The analytical results obtained with acetylresoflavin, m. p. 275—279°, and methylresoflavin agree with the formulæ

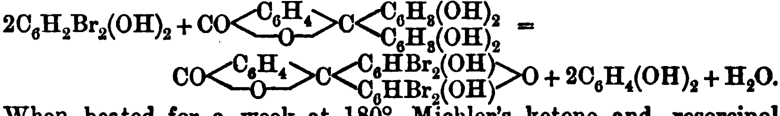
$$C_{14}H_8O_4(OAc)_3 \text{ and } C_{14}H_8O_4(OMe)_3$$

respectively.

The dye formed by the action of ammonium persulphate on ethyl 3:5-dihydroxybenzoate is probably impure resoflavin. The product obtained by the action of ammonium persulphate on gallic acid yields with methyl iodide and potassium hydroxide a white, crystalline product, $C_{14}HO_2(OMe)_9$, m. p. 84—87°. The interrelations of these substances require further investigation. G. Y.

Catecholphthalein. Richard Meyer and Hermann Pfotenhauer (*Ber.*, 1907, **40**, 1442—1445).—On condensing catechol with phthalic anhydride in the presence of zinc chloride, Baeyer and Kochendörfer (Abstr., 1889, 1153) obtained catecholphthalein as a brown, uncrystallisable mass. This phthalein has been obtained crystalline by digestion with water and animal charcoal twice and afterwards purifying the yellowish-white needles so obtained by boiling with benzene which dissolves the catechol. It has no definite m. p., but sinters at 80—90°, dissolves more easily in water than other phthaleins, and is volatile in steam. The fact that catechol yields a phthalein, whereas resorcinol and quinol form dihydroxy-fluorans is thus confirmed. The *acetate*, $C_{20}H_{10}O_2(OAc)_4$, crystallises in white needles, m. p. 155—156°. W. R.

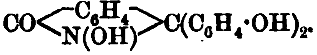
Mutual Exchange of Aromatic Complexes. Richard Meyer and Hermann Pfotenhauer (*Ber.*, 1907, **40**, 1445—1450).—Eosin is obtained when dibromoresorcinol in the form of dibromo-β-resorcylic acid is heated with catecholphthalein and zinc chloride at 170° for two to three hours (compare Abstr., 1906, i, 23); the exchange of complexes therefore takes place in accordance with the equation



$$2C_6H_2Br_2(OH)_2 + CO{<}\begin{matrix}C_6H_4\\ O\end{matrix}{>}C{<}\begin{matrix}C_6H_8(OH)_2\\ C_6H_8(OH)_2\end{matrix} = CO{<}\begin{matrix}C_6H_4\\ O\end{matrix}{>}C{<}\begin{matrix}C_6HBr_2(OH)\\ C_6HBr_2(OH)\end{matrix}{>}O + 2C_6H_4(OH)_2 + H_2O.$$

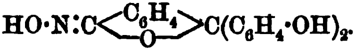
When heated for a week at 180°, Michler's ketone and resorcinol yield dimethylaniline, and, in the place of the expected 3:6-dihydroxyxanthone, a *substance*, $C_{16}H_{20}O_8N_2$, m. p. 238—239°, which is a by-product, resulting probably by the action of the dimethylaniline on the dihydroxyxanthone; the latter, however, cannot be isolated. C. S.

Reduction Product of Phenolphthaleinoxime. Richard Meyer and J. Glikin (*Ber.*, 1907, **40**, 1454—1458).—The behaviour of the reduction product of phenolphthaleinoxime (compare Friedländer, Abstr., 1893, i, 273) is in agreement with the formula $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}OH)_2$; the oxime itself would be



$$CO{<}\begin{matrix}C_6H_4\\ N(OH)\end{matrix}{>}C(C_6H_4{\cdot}OH)_2.$$

The unexpected stability of phthaleinanilides to reducing agents (following abstract), however, speaks against analogous formulæ for the oxime and the anilide; for the former is suggested the formula



$HO{\cdot}N{:}C{<}\begin{smallmatrix}C_6H_4\\ O\end{smallmatrix}{>}C(C_6H_4{\cdot}OH)_2$.

The reduction product of phenolphthaleinoxime does not form an ester by treatment with alcohol and hydrogen chloride; it does yield, however, the following ethers. The *methyl ether*,

$$NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}OH){\cdot}C_6H_4{\cdot}OMe,$$

obtained by the action of sodium methoxide and excess of methyl iodide in methyl-alcoholic solution, has m. p. 236—237°; the *dimethyl ether*, $NH_2{\cdot}CO{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}OMe)_2$, m. p. 130—131°, is obtained by the action of sodium hydroxide and methyl sulphate; the *diethyl ether*, prepared in a similar manner to the methyl ether, has m. p. 125—126°; the *dibenzyl ether* has m. p. 158°. The diacetate and the dibenzoate have been prepared by Herzig and Meyer (Abstr., 1897, i, 69).

Attempts to prepare the reduced oxime by replacing OEt by NH_2 in the ester of phthalin, $CO_2Et{\cdot}C_6H_4{\cdot}CH(C_6H_4{\cdot}OH)_2$, were unsuccessful.

C. S.

Behaviour of Phthaleinanilides to Reducing Agents. RICHARD MEYER and KURT LANGE (*Ber.*, 1907, **40**, 1459—1462).—The anilides of diphenylphthalide, fluoran, phenolphthalein, and fluorescein are practically unattacked by potassium hydroxide and zinc dust in boiling alcoholic solution. C. S.

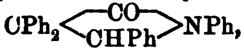
Quinic Acid. GUSTAV KNÖPFER (*Arch. Pharm.*, 1907, **245**, 77—80).—Unlike Echtermeier (Abstr., 1906, i, 367, 368), the author succeeded in preparing a crystalline ammonium salt, amide, and anilide (m. p. 183°; already prepared by Hesse, with m. p. 174°) of quinic acid. *Ammonium quinate*, $C_7H_{15}O_6N$, m. p. 179°, was obtained by triturating quinic acid with solid ammonium carbonate and volatilising the excess of carbonate on the water-bath. *Quinamide*, $C_7H_{13}O_5N$, m. p. 132°, was obtained by heating ethyl quinate with alcoholic ammonia at 125° for six hours.

Methyl methylquinate and *ethyl ethylquinate*, $C_{11}H_{20}O_6$, were obtained by heating lead quinate with methyl or ethyl iodide respectively at 125° for six hours; both are viscid liquids which decompose when distilled even under diminished pressure. C. F. B.

Condensation of Aldehydes with Phenolcarboxylic Acids. E. HÖST MADSEN (*Arch. Pharm.*, 1907, **245**, 42—48).—Formaldehyde and benzaldehyde condense with salicylic acid in the presence of hydrogen chloride in accordance with the equation $CHRO + 2OH{\cdot}C_6H_4{\cdot}CO_2H = CHR[C_6H_3(OH){\cdot}CO_2H]_2 + H_2O$ [$R = H$ and Ph respectively]; the condensation appears to take place in the para position to the OH group. In the first case the reacting substances were boiled in aqueous solution, in the second they were heated at 160° in a sealed tube without water; in both cases special precautions had to be taken in order to obtain a crystalline product.

Methanedisalicylic (methylenedisalicyclic) *acid*, $C_{15}H_{12}O_6$, melts at 243—244° and loses carbon dioxide at 180°. *Phenylmethanedisalicylic acid*, $C_{21}H_{16}O_6$, melts at 242—245° and loses carbon dioxide at 130—150°; its *diacetyl* derivative, $C_{25}H_{20}O_8,H_2O$, melts at 124° and begins to decompose at 101°. C. F. B.

Ketens. IV. Reactions of Diphenylketen. HERMANN STAUDINGER (*Ber.*, 1907, 40, 1145—1148. Compare Abstr., 1905, i, 444; 1906, i, 234, 861).—A solution of diphenylketen in ether or light petroleum reacts with water, alcohol, or amines, yielding diphenylacetic acid, its esters, or amides. The keten forms additive compounds with tertiary amines; the only one isolated was the *quinoline* compound, $2C_{14}H_{10}O,C_9H_7N$, m. p. 121—122°, which is completely dissociated in chloroform solution. It also combines with unsaturated compounds, for example, with *cyclo*pentadiene, yielding a *product*, $C_{14}H_{10},C_5H_6$, m. p. 89—90°, and with quinone, forming a compound, $C_{14}H_{10}O,C_6H_4O_2$, which crystallises from acetone in colourless prisms, m. p. 143°. With benzylideneaniline it yields the *β-lactam*,



$$CPh_2<\begin{matrix}CO\\CHPh\end{matrix}>NPh,$$

m. p. 159—160°, which on hydrolysis with aqueous alcoholic potassium hydroxide yields the *β-anilino-acid*, $NHPh\cdot CHPh\cdot CPh_2\cdot CO_2H$, m. p. 122—123°.

The keten does not polymerise, and with magnesium phenyl bromide yields triphenylvinyl alcohol.

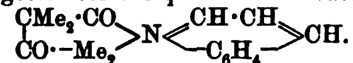
The keten may be prepared by the action of tertiary bases on diphenylacetyl chloride. J. J. S.

Ketens. V. Dimethylketen. HERMANN STAUDINGER and H. W. KLEVER (*Ber.*, 1907, 40, 1149—1153. Compare Abstr., 1906, i, 234).—Among the products formed during the preparation of dimethylketen is a liquid bimolecular polymeric compound, $(C_4H_6O)_2$, b. p. 170—171°. It has an odour of peppermint, and with sodium hydroxide solution yields an acid readily soluble in water. The *phenylhydrazone*, $C_{14}H_{18}ON_2$, melts at 66—67°. The keten forms additive compounds with tertiary bases; these are extremely stable, do not give the characteristic reaction of the keten, and are not affected by oxygen. *Dimethylketen-quinoline*, $C_9H_7N,2C_4H_6O$, forms colourless crystals from light petroleum, m. p. 81—82°, and when boiled for a short time with mineral acids or heated with water at 120° it yields an acid,

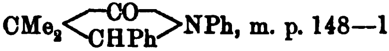
$$2C_4H_6O,C_9H_7N,H_2O,$$

m. p. 152—153°, which is completely hydrolysed to quinoline and *iso*butyric acid with hot hydrochloric acid. The *ethyl* ester has m. p. 60·5—61·5°; *methyl* ester, 58—59°, and the *anilide* 109—110°. *Dimethylketen-quinaldine*, $2C_4H_6O,C_{10}H_9N$, has m. p. 119·5—120·5°, and di-*methylketen*-p-*toluquinaldine*, 129—130°. Both are less stable than the quinoline derivative. When carefully boiled with dilute acetic acid the quinaldine derivative yields an *acid*, $2C_4H_6O,C_{10}H_9N,H_2O$, m. p. 137—138°. *Dimethylketen-acridine*, $2C_4H_6O,C_{13}H_9N$, melts at 127—128° and is very stable. *Dimethylketen-pyridine* is an unstable oil and readily yields the corresponding *acid*, m. p. 84—96°.

The formula suggested for the quinoline derivative is



$$\begin{matrix}CMe_2\cdot CO\\ CO\cdot{-}Me_2\end{matrix}>N<\begin{matrix}CH\cdot CH\\ C_6H_4\end{matrix}>CH.$$

With benzylideneaniline the keten yields an additive compound, namely, a *β-lactam*,  $CMe_2<\begin{matrix}CO\\ CHPh\end{matrix}>NPh$, m. p. 148—149°.

J. J. S.

Condensation of Piperil with Benzaldehyde and Ammonia. T. Nowosielski (*Bull. Acad. Sci., Cracow*, 1906, 276—278).—The formation of a glyoxaline derivative by condensation of piperil with benzaldehyde and ammonia, according to the general reaction of α-diketones, offered some points of interest, as in many respects piperil differs from its analogue benzil.

An attempt to prepare piperil by oxidation of piperoin with nitric acid resulted in the formation of a *dinitropiperil*,

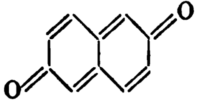
$$CH_2{:}O_2{:}C_6H_2(NO_2)\cdot CO\cdot CO\cdot C_6H_2(NO_2){:}O_2{:}CH_2,$$

which separates as a yellow crust.

The *glyoxaline* derivative (*piperilbenzoline*), $C_3N_2HPh(C_6H_3{:}O_2{:}CH_2)_2$, formed by the action of ammonia on piperil and benzaldehyde in alcoholic solution at 60—70°, crystallises in microscopic plates or long needles, m. p. 251—253°, and, on exposure to air in alcoholic potassium hydroxide solution, yields benzoic and piperonylic acids and ammonia. The *hydrochloride*, $C_{23}H_{16}O_4N_2,HCl$, forms small, white needles; the *platinichloride*, $(C_{23}H_{16}O_4N_2)_2,H_2PtCl_6$, is obtained as a crystalline precipitate.

G. Y.

Quinonoid Compounds. XI. 2:6-Naphthaquinone. Richard Willstätter and Jakob Parnas (*Ber.*, 1907, 40, 1406—1415).—amphi- *or* 2:6-*Naphthaquinone*, prepared by the oxidation of the corresponding quinol in dry benzene solution with lead peroxide in large excess, crystallises from a mixture of benzene and petroleum in small, reddish-yellow prisms changing colour suddenly at 130—135°. The quinone is stable in air, odourless, and non-volatile, thus resembling *o*-quinones. In its chemical behaviour, it resembles *p*-benzoquinone rather than the 1 : 2- or 1 : 4-naphthaquinones in the ease with which it passes back into an aromatic substance. A table is given demonstrating this, comparing these quinones with regard to their oxidising action on cold very dilute hydriodic acid, hydrocœrulignone, hæmatoxylin, sulphurous acid, ferrous ferrocyanide, and guaiacol resin solution. That the substance is 2:6-naphthaquinone and not a dinaphthalene derivative is shown by its reduction to 2:6-dihydroxynaphthalene by cold dilute hydriodic acid; and the conclusion is supported by a molecular weight determination in benzene by the boiling point method. The small reactivity of the α- and β-naphthaquinones as compared with this substance is, perhaps, due to the *amphi*-derivative being a true naphthaquinone, the other two affecting only one ring of the naphthalene and therefore being "incomplete." *as-α*-Tetrahydronaphthaquinone (Bamberger and Lengfeld, Abstr., 1890, 1305) is analogous to *p*-benzoquinone in its behaviour towards hydriodic acid and hydrocœrulignone.

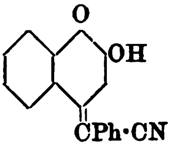


amphi-*Naphthaquinonehydrone*, $C_{20}H_{14}O_4$, the additive product obtained by mixing the benzene solution of quinone and corresponding quinol in ether, crystallises in dark bluish-green, microscopic needles which suddenly decolorise at 124—125° without melting. It is more unstable than the quinone.

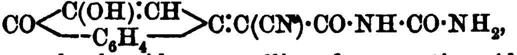
1·08 Gram of 2 : 6-dihydroxynaphthalene, m. p. 218° (corr.) (Emmert, Abstr., 1888, 57; m. p. 215—216°), dissolves in 1 litre of water at 14°. 2 : 6-*Dimethoxynaphthalene*, $C_{12}H_{12}O_2$, m. p. 150°, crystallises in rhombic plates from benzene. W. R.

Condensations with 1 : 2-Naphthaquinone-4-sulphonic Acid. II.

Franz Sachs, Erich Berthold, and Bruno Zaar (*Zeitsch. Farb.-Ind.*, 1907, **6**, 62—68 and 81—84. Compare Abstr., 1905, i, 909).—1 : 2-Naphthaquinone-4-sulphonic acid is an extraordinarily active substance, condensing not only with amino-compounds but also with compounds containing a methyl or methylene group (compare Ehrlich and Herter, Abstr., 1904, i, 598). In all cases the sulphonic radicle is displaced and a derivative of 2 hydroxy-α-naphthaquinone obtained; thus, for example, benzyl cyanide gives the annexed compound. The condensation of 1 : 2-naphthaquinone-4-sulphonic acid (in the form of its potassium salt) with different substances gives rise to the compounds described below.

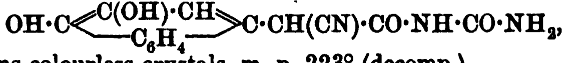


2-*Hydroxy*-1 : 4-*naphthaquinone-4-carboxycyanomethide carbamide*,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{C(OH){:}CH}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{C{:}C(CN)\cdot CO\cdot NH\cdot CO\cdot NH_2}$$

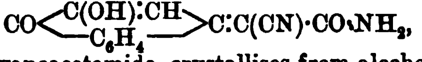
prepared from cyanoacetylcarbamide, crystallises from acetic acid in orange-red needles, m. p. 303°, and on reduction with zinc dust and acetic acid gives 1 : 2-*dihydroxynaphthyl-4-cyanoacetylcarbamide*,



$$\mathrm{OH\cdot C}\left<\begin{matrix}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{C\cdot CH(CN)\cdot CO\cdot NH\cdot CO\cdot NH_2},$$

which forms colourless crystals, m. p. 223° (decomp.).

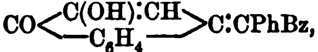
2-*Hydroxy*-1 : 4-*naphthaquinone-4-cyanomethide carboxylamide*,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{C(OH){:}CH}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{C{:}C(CN)\cdot CO\cdot NH_2},$$

prepared from cyanoacetamide, crystallises from alcohol or acetic acid in yellow needles, m. p. 227—228°.

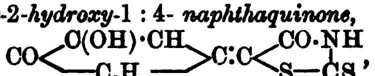
2-*Hydroxy*-1 : 4-*naphthaquinone-4-phenylbenzoylmethide*,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{C(OH){:}CH}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{C{:}CPhBz},$$

prepared from deoxybenzoin, crystallises from acetic acid in orange-red prisms, m. p. 179°.

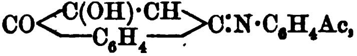
4-*Rhodanylidene-2-hydroxy*-1 : 4- *naphthaquinone*,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{C{:}C}\left<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{S{-}CS}\end{matrix}\right.,$$

prepared from rhodanic acid, crystallises from glacial acetic acid in dark red needles, m. p. 290°.

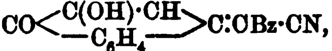
2-*Hydroxy*-1 : 4-*naphthaquinone*-4-p-*acetophenylimide*,



$$\mathrm{CO}\left<\begin{matrix}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{matrix}\right>\mathrm{C{:}N\cdot C_6H_4Ac},$$

prepared from *p*-aminoacetophenone, crystallises from alcohol in rose-red, rhombic plates, m. p. 235—240°.

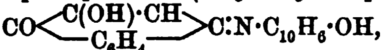
2-*Hydroxy*-1 : 4-*naphthaquinone*-4-*benzoylcyanomethide*,



$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{C(OH)\cdot CH}}{\mathrm{C_6H_4}}{>}\mathrm{C{:}CBz\cdot CN},$$

prepared from cyanoacetophenone, crystallises from alcohol or acetic acid in long, yellowish-red needles, m. p. 257°.

2-*Hydroxy*-1 : 4-*naphthaquinone*-4-(2′-*hydroxy*-7′-*naphthyl*)*imide*,

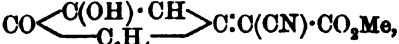


$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{C(OH)\cdot CH}}{\mathrm{C_6H_4}}{>}\mathrm{C{:}N\cdot C_{10}H_6\cdot OH},$$

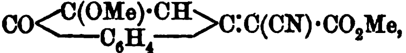
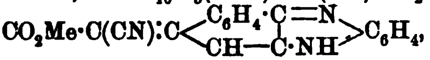
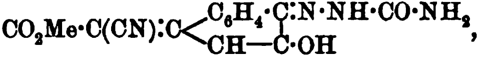
obtained from 2 : 7-aminonaphthol, crystallises from alcohol on adding water; m. p. 290°. On reduction with zinc dust in hot acetic acid containing acetic anhydride and sodium acetate, 1 : 2 : 7′-*triacetoxydinaphthylamine*, $\mathrm{OAc\cdot C_{10}H_6\cdot NH\cdot C_{10}H_5(OAc)_2}$, is obtained in colourless needles, m. p. 204—205°.

2-*Hydroxy*-1 : 4-*naphthaquinone*-4-(1′-*hydroxy*-5′-*naphthyl*)*imide*, prepared from 1 : 5-aminonaphthol, crystallises from dilute alcohol.

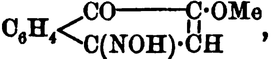
2-*Hydroxy*-1 : 4-*naphthaquinone*-4-*cyanocarboxymethylmethide*,



$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{C(OH)\cdot CH}}{\mathrm{C_6H_4}}{>}\mathrm{C{:}C(CN)\cdot CO_2Me},$$

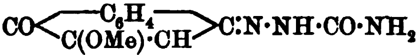
prepared from methyl cyanoacetate, crystallises from alcohol in silky, yellow needles, m. p. 164°; on methylation with diazomethane the *methyl ether*,  $\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{C(OMe)\cdot CH}}{\mathrm{C_6H_4}}{>}\mathrm{C{:}C(CN)\cdot CO_2Me}$, is obtained, which forms bright yellow, silky needles, m. p. 155°, and on reduction with zinc and acetic acid gives *methyl* 1-*hydroxy*-2-*methoxy*-4-*naphthylcyanoacetate*, $\mathrm{OH\cdot C_{10}H_5(OMe)\cdot CH(CN)\cdot CO_2Me}$, m. p. 128°. The *eurhodole*,  $\mathrm{CO_2Me\cdot C(CN){:}C}{<}\genfrac{}{}{0pt}{}{\mathrm{C_6H_4\cdot C{=}N}}{\mathrm{CH{-}C\cdot NH}}{>}\mathrm{C_6H_4}$, prepared from the foregoing methide by the action of *o*-phenylenediamine, crystallises from alcohol in violet-brown, lanceolate needles, m. p. 179°. The *semicarbazone*,  $\mathrm{CO_2Me\cdot C(CN){:}C}{<}\genfrac{}{}{0pt}{}{\mathrm{C_6H_4\cdot C{:}N\cdot NH\cdot CO\cdot NH_2}}{\mathrm{CH{-}C\cdot OH}}$, separates from alcohol or acetic acid in yellowish-brown, hexagonal crystals, m. p. 261°.

Attempts to prepare the oxime of methyl 1-hydroxy-2-methoxy-4-naphthylcyanoacetate by the action of hydroxylamine caused the elimination of the cyanoacetyl group, the *monoxime*,



$$\mathrm{C_6H_4}{<}\genfrac{}{}{0pt}{}{\mathrm{CO{-}C\cdot OMe}}{\mathrm{C(NOH)\cdot CH}},$$

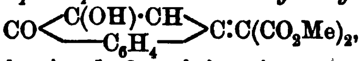
of 2-methoxy-1 : 4-naphthaquinone being obtained; this substance can also be prepared by the action of hydroxylamine on 2-methoxy-1 : 4-naphthaquinone, and crystallises from alcohol in yellowish-white prisms or needles, m. p. 228° with decomposition. 2-*Methoxy*-1 : 4-*naphthaquinone*, obtained by methylating 2-hydroxy-1 : 4-naphthaquinone, crystallises from alcohol in yellow needles and melts at 146—147°; the *semicarbazone*,



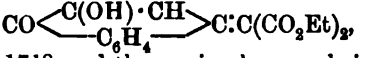
$$\mathrm{CO}{<}\genfrac{}{}{0pt}{}{\mathrm{C_6H_4}}{\mathrm{C(OMe)\cdot CH}}{>}\mathrm{C{:}N\cdot NH\cdot CO\cdot NH_2},$$

crystallises from acetic acid in golden needles, m. p. 237—238°.

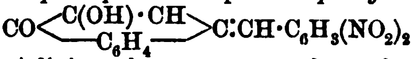
2-*Hydroxy*-1 : 4-*naphthaquinone*-4-*dicarboxymethylmethide*,



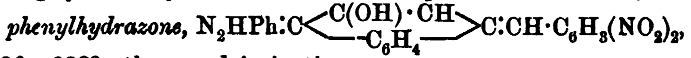
$$\mathrm{CO}<\begin{array}{c}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}C(CO_2Me)_2},$$

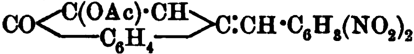
is obtained by condensing 1 : 2-naphthaquinone-4-sulphonic acid with methyl malonate, and has m. p. 130°; the *oxime* forms yellowish-brown prisms, m. p. 194°, and the semicarbazone, canary-yellow needles, m. p. 199°. The *oxime* of the corresponding diethyl compound,  $\mathrm{CO}<\begin{array}{c}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}C(CO_2Et)_2}$, forms greenish-yellow crystals, m. p. 171°, and the semicarbazone, bright yellow needles, m. p. 174°.

2-*Hydroxy*-1 : 4-*naphthaquinone*-4-op-*dinitrophenylmethide*,

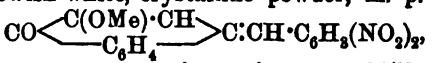
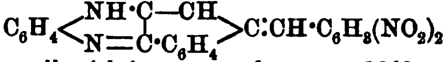


$$\mathrm{CO}<\begin{array}{c}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}CH\cdot C_6H_3(NO_2)_2},$$

prepared from 2 : 4-dinitrotoluene, separates from glacial acetic acid in orange-yellow crystals, melts and decomposes at 238—240°, and gives a *phenylhydrazone*,  $\mathrm{N_2HPh{:}C}<\begin{array}{c}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}CH\cdot C_6H_3(NO_2)_2}$, m. p. 286—288°; the *acetyl* derivative,

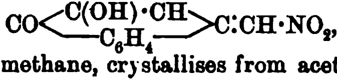


$$\mathrm{CO}<\begin{array}{c}\mathrm{C(OAc)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}CH\cdot C_6H_3(NO_2)_2}.$$

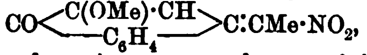
forms a yellowish-white, crystalline powder, m. p. 187·5—188°, the *methyl ether*,  $\mathrm{CO}<\begin{array}{c}\mathrm{C(OMe)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}CH\cdot C_6H_3(NO_2)_2}$, crystallises from acetone in lustrous, orange prisms, sinters at 207°, and melts at 216°. The *eurhodole*,  $\mathrm{C_6H_4}<\begin{array}{l}\mathrm{NH\cdot C{-}CH}\\ \mathrm{N{=}C\cdot C_6H_4}\end{array}>\mathrm{C{:}CH\cdot C_6H_3(NO_2)_2}$, separates from acetic acid as a yellowish-brown powder, m. p. 180°.

2-*Hydroxy*-1 : 4-*naphthaquinone*-4-sym.-*trinitrophenylmethide*, prepared from 2 : 4 : 6-trinitrotoluene, crystallises from glacial acetic acid in thick, yellow needles, m. p. 260°.

2-*Hydroxy*-1 : 4-*naphthaquinone*-4-*nitromethide*,



$$\mathrm{CO}<\begin{array}{c}\mathrm{C(OH)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}CH\cdot NO_2},$$

prepared from nitromethane, crystallises from acetone on adding light petroleum in small, yellow needles, m. p. 153—156°, and is very sensitive to light; methylation with diazomethane gives not a mono-methyl derivative but 2-*methoxy*-1 : 4-*naphthaquinone*-4-*methylnitromethide*,  $\mathrm{CO}<\begin{array}{c}\mathrm{C(OMe)\cdot CH}\\ \mathrm{C_6H_4}\end{array}>\mathrm{C{:}CMe\cdot NO_2}$, m. p. 160°.

All the foregoing compounds, containing a hydroxyl group in the ortho-position to the chromophore, are mordant dyes, thus confirming Möhlau and Steimmig's rule (*Zeitsch. Farb.-Ind.*, 3, 35) that a hydroxyl group in this position suffices to produce a mordant dye. The tinctorial properties of the compounds enumerated are described in detail.

W. A. D.

1 : 6-Dihydroxyanthraquinone. OTTO FROBENIUS and EDUARD HEPP (*Ber.*, 1907, 40, 1048—1051).—1 : 6-Dihydroxyanthraquinones have been described by Farbwerke vorm. Meister, Lucius, and Brüning, and by Wedekind and Co.; the former product is shown to be a pure substance and the latter to be a mixture containing *iso*anthraflavic acid in quantity.

1:6-Dihydroxyanthraquinone, m. p. 271—272° (not 260° as previously stated), crystallises in orange-yellow needles, and gives a red coloration in concentrated sulphuric acid solution; the *barium* and *calcium* salts are insoluble even in hot water. The *diacetate*, m. p. 205—206°, and *dibenzoate*, m. p. 209—211°, crystallise in citron-yellow needles. Flavopurpurin alone and no hydroxyanthrarufin are produced on oxidation. The compound, erythrohydroxyanthraquinonesulphonic anhydride, obtained by Lifschütz (Abstr., 1884, 1189) from α-nitroanthraquinonesulphonic acid and potassium nitrite is in reality diazoanthraquinonesulphonic acid. Wedekind and Co.'s product has m. p. 405°; diacetate, m. p. 228°; dibenzoate, m. p. 232—233°.

E. F. A.

Preparation of the Bornyl Esters of the Aromatic Hydroxycarboxylic Acids. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 175097).—The bornyl esters having the general formula

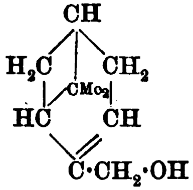
$$C_{10}H_7O{\cdot}CO{\cdot}R{\cdot}OH,$$

where R is an aromatic group, are of importance in therapeutics and in the preparation of borneol. They may be prepared by warming an aromatic hydroxycarboxylic acid with a terpene such as pinene or camphene or a mixture of these hydrocarbons with or without a condensing agent.

"*Bornyl*" *salicylate*, $C_{10}H_7O{\cdot}CO{\cdot}C_6H_4{\cdot}OH$, b. p. 171—173°/5 mm., which is employed medicinally under the name of "salit," is obtained by heating a mixture of salicylic acid and French oil of turpentine, first at 110° and then gradually to 150°. After removing the unchanged reagents, the ester was obtained as a slightly coloured oil having a faint taste and odour; it is soluble in the ordinary organic media and develops a violet coloration with alcoholic ferric chloride. Its alkali salts are solid, unstable substances readily hydrolysing to yield sodium salicylate and a mixture of borneol and *iso*borneol. The pure bornyl ester is obtained when pure pinene is employed, whilst pure camphene yields the corresponding *iso*bornyl ester. G. T. M.

Myrtenol, a Primary Alcohol, $C_{10}H_{16}O$, from the Ethereal Oil of Myrtus Communis. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 1363—1378).—The ethereal oil from *Myrtus communis* contains in the fractions of high-boiling point an alcohol, $C_{10}H_{16}O$, which is designated as myrtenol; this is a dicyclic primary alcohol, containing one double linking, and has the pinene structure. A dextrorotatory pinene can be prepared from it. When oxidised by potassium permanganate, myrtenol forms an optically active dibasic pinic acid. When oxidised by chromic acid, it forms the aldehyde, $C_{10}H_{14}O$, from which the oxime, $C_{10}H_{14}{:}N{\cdot}OH$, was obtained; the latter yields the nitrile, $C_{10}H_{13}N$, an acid, $C_{10}H_{14}O_2$, and a reduced acid, $C_{10}H_{16}O_2$. The latter compounds are the first representatives of the dicyclic unsaturated or saturated series of the pinene system.

In addition to myrtenol, the following are present in the ethereal oil examined: cineol, pinene, dipentene, and camphor. After fractionation, the myrtenol was separated by converting it into *myrtenyl hydrogen phthalate*, $CO_2H{\cdot}C_6H_4{\cdot}CO_2C_{10}H_{15}$, with m. p. 114—115° and $[\alpha]_D$ +21·36° in ethyl-alcoholic solution ($c = 50$) (temperature not quoted). When an excess of alkali is added, the myrtenol may be distilled off in a current of steam.

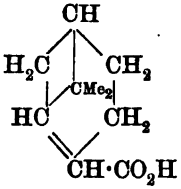


Myrtenol has b. p. 102·5°/9 mm., 222—224°/760 mm., D^{20} 0·9763, n_D 1·49668, α_D +45°45′ ($l = 1$), and is the first example of a primary dicyclic alcohol.

Myrtenyl chloride, $C_{10}H_{15}Cl$, obtained by the action of phosphorus pentachloride on myrtenol in light petroleum solution, has b. p. 90°/12 mm., D^{20} 1·015, n_D 1·49762. When reduced by sodium and ethyl alcohol, it forms a dextrorotatory pinene, with α_D + 28° ($l = 1$), which was identified by conversion into a number of derivatives.

Myrtenyl ethyl ether, $C_{10}H_{15}OEt$, obtained along with pinene by the reduction of myrtenyl chloride, has b. p. 80—85°/10 mm., D^{20} 0·899, and n_D 1·4725.

When myrtenol is oxidised in glacial acetic acid solution it is converted into *myrtenal*, $C_{10}H_{14}O$, which has b. p. 87—90°/10 mm., D^{20} 0·9876, n_D 1·50420, and forms an *oxime*, $C_{10}H_{15}ON$, which crystallises from ethyl alcohol and has m. p. 71—72; when boiled with an excess of acetic anhydride, this oxime yields a *nitrile*, $C_{10}H_{13}N$, b. p. 100—102°/10 mm., D^{20} 0·967, n_D 1·49192, α_D + 44°30′ ($l = 1$). When this *nitrile* is saponified by alcoholic potassium hydroxide it is converted into *myrtenic acid*, $C_{10}H_{14}O_2$, with b. p. 148°/9 mm. and m. p. 54°. Its *methyl ester* has b. p. 99°/9 mm., D^{20} 1·022, and n_D 1·48616.



Dihydromyrtenic acid, obtained by the reduction of myrtenic acid with sodium and amyl alcohol, has b. p. 142—144°/8 mm., D 1·049, and n_D 1·48519. Towards potassium permanganate it behaves like a saturated acid.

When myrtenol is oxidised by potassium permanganate it is converted into a dextrorotatory *pinic acid*, $C_9H_{14}O_4$, b. p. 212—216°/10 mm. Its *dimethyl ester*, $C_{11}H_{18}O_4$, has b. p. 121—124°/10 mm., D^{20} 1·0582, n_D 1·44962, and α_D + 13°50′ ($l = 1$). Its *diethyl ester*, $C_{13}H_{22}O_4$, has b. p. 142—146°/10 mm., D^{20} 1·0104, n_D 1·44962, and α_D + 8° (length of tube and temperature not quoted).

Myrtenyl formate, $C_{11}H_{16}O_2$, has b. p. 93—97°/10 mm., D^{20} 1·009, and n_D 1·47936. The *acetate*, $C_{12}H_{18}O_2$, has b. p. 105—107°/9 mm., D^{20} 0·9865, and n_D 1·47838. When this ester is saponified by alcoholic potassium hydroxide the recovered myrtenol has the same rotation as before.

When myrtenol is heated with dilute sulphuric acid, a hydrocarbon, $C_{10}H_{14}$, is formed, having b. p. 55°/9 mm., D^{20} 0·858, and n_D 1·49097; it is optically inactive and is probably *p*-cymene. The 4-ring in myrtenol is not so easily broken as that in pinene.

A. McK.

Santalol. FRIEDRICH W. SEMMLER and KURT BODE (*Ber.*, 1907, **40**, 1124—1145. Compare following abstract; Chapman and Burgess, Trans., 1901, **79**, 134; Guerbet, Abstr., 1900, i, 242, 401).—The primary alcoholic nature of santalol has been proved by its oxidation to *santalaldehyde*, $C_{15}H_{22}O$, by means of an acetic acid solution of chromic acid. The pure aldehyde, prepared from the semicarbazone by decomposing it slowly with phthalic anhydride, has b. p. 152—155°/10 mm., D^{20} 0·995, n_D 1·51066, and is dextrorotatory. The *semicarbazone*, $C_{16}H_{25}ON_3$, after recrystallisation from methyl alcohol, has m. p. 230°. Other products are also formed during the oxidation of santalol, these are lævorotatory, but have not been obtained in a pure state. d-*Santaloloxime*, $C_{15}H_{23}ON$, has m. p. 104—105° and b. p. 182—185°/10 mm., and with acetic anhydride yields a *nitrile*, $C_{15}H_{21}N$, b. p. 162—166°/9 mm., D^{20} 0·990, n_D 1·5033, and $a_D + 14°$ (100 mm. tube). On hydrolysis the nitrile yields *santalic acid*, $C_{15}H_{22}O_2$, in the form of a viscid oil, b. p. 192—195°/9 mm. Its *copper* and *silver* salts are soluble and its *methyl* ester has b. p. 160—164°/10 mm., D^{20} 1·002, and n_D 1·49097.

Santalyl chloride, $C_{15}H_{23}Cl$, obtained by the action of phosphorus pentachloride on a light petroleum solution of santalol, has b. p. 147—155°/10 mm. and D^{20} 1·0398; when reduced with sodium and alcohol it yields a sesquiterpene, *γ-santalene*, $C_{15}H_{24}$, b. p. 118—120°/9—10 mm., D^{20} 0·9355, n_D 1·5042.

Santalol is not reduced by sodium and alcohol, but with hydriodic acid and phosphorus yields a hydrocarbon, $C_{15}H_{26}$, b. p. 125—130°/12 mm., D^{20} 0·8999, and n_D 1·48712.

Oxidation of santanol with permanganate in neutral solution yields a small amount of *dihydroxydihydrosantalol* (*santalolglycerol*), $C_{15}H_{26}O_3$, b. p. 215—220°/10 mm., together with tricyclo*eksantalic acid*, $C_{11}H_{16}O_2$ (compare following abstract). The acid is the chief product when 10 equivalents of oxygen are used. It has m.p. 71—72°, b. p. 165—167°/10 mm., D^{25} 1·071. The *copper* and *silver* salts are insoluble, the *amide* melts at 106°, the *methyl* ester has b. p. 125—128°/10 mm., D^{20} 1·0164, n_D 1·47838, and its rotation like that of the acid varies considerably. tricyclo*Eksantalol*, $C_{11}H_{18}O$, obtained by reducing the methyl ester with sodium and absolute alcohol, has b. p. 130—132°/10 mm., D^{20} 0·9859, n_D 1·49478, and the corresponding tricyclo *eksantalaldehyde*, $C_{11}H_{16}O$, b. p. 125—130°/13 mm., D^{20} 1·012, n_D 1·498.

When oxidised with ozone in benzene solution, sanatol yields *tricyclo*-eksantalic acid, which is quite stable towards permanganate or ozone. The acid is also unaffected when its vapour mixed with carbon dioxide is passed over reduced copper at 500°, or when the acid is fused with potassium hydroxide, but when the calcium salt is distilled a hydrocarbon, $C_{10}H_{14}$, resembling cymene is obtained together with an *aldehyde*, $C_{11}H_{16}O$, the *semicarbazone* of which has m. p. 189—192°.

A considerable amount of *tricyclo*eksantalaldehyde is also formed during the oxidation of santalol with ozone. The *semicarbazone*,

$$C_{11}H_{16}:N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

melts at about 156° and may be used for regenerating the pure aldehyde. The *oxime*, $C_{11}H_{16}$:N·OH, has b. p. 140—150°/10 mm., D^{20} 1·03, n_D 1·506, and α_D +1°. The *nitrile* of *tricyclo*eksantalic acid has b. p. 114—120°/10 mm., D^{20} 1·002, n_D 1·4881, α_D +6° (100 mm. tube). The mother substance of the whole series of compounds, namely, *nor*tricyclo*eksantalane*, $C_{10}H_{16}$, is obtained when the ozonide of santalol is distilled under reduced pressure, b. p. 57—59°/9 mm. or 183·5°/767 mm., D^{20} 0·885, n_D 1·46856, α_D −11°. Acids of low boiling point are also formed from the ozonide.

Most of these tricyclo-derivatives can be converted into dicyclic, unsaturated compounds. When a solution of *tricyclo*eksantalic acid in methyl alcohol is saturated with hydrogen chloride and kept for some time the *methyl* ester of *hydrochloro*dicyclo*eksantalic acid*, $C_{12}H_{18}O_2$,HCl, is formed, b. p. 154—156°/9—10 mm., D^{20} 1·101, n_D 1·496, α_D +17°. When boiled with alcoholic potassium hydroxide the ester yields dicyclo*eksantalic acid*, $C_{11}H_{16}O_2$, m. p. 64°, b. p. 164—166°/9 mm., $[\alpha]_D$ −41·81 in alcoholic solution. The *methyl* ester, $C_{12}H_{18}O_2$, has b. p. 125—128°/9 mm., D^{20} 1·0191, n_D 1·48809, and α_D −27° (100 mm. tube). The dicyclic unsaturated nature of the acid follows (*a*) from its behaviour towards permanganate and ozone, both of these reagents readily react with the acid yielding acids of different boiling points, and (*b*) from its molecular refraction. When the methyl ester is reduced with sodium and alcohol, it yields dicyclo*eksantalol*, $C_{11}H_{18}O$, b. p. 130—134°/9 mm., D^{20} 0·9791, n_D 1·50051, and α_D −22°.

dicyclo*Eksantalane*, $C_{10}H_{15}Me$, is obtained when *tricyclo*eksantalol is treated with phosphorus pentachloride in light petroleum solution and the resulting chloride reduced with sodium and alcohol. *Eksantalyl chloride* has b. p. 110—114°/10 mm., D^{20} 1·0083, and n_D 1·47348. The hydrocarbon has b. p. 72—74°/10 mm., D^{20} 0·871, and n_D 1·4774. The value of the molecular refraction agrees with that required for a dicyclic system.

*Chlorodihydronor*dicyclo*eksantalane*, $C_{10}H_{17}Cl$, is formed when nor*tricyclo*eksantalane is dissolved in methyl alcohol, the solution saturated with hydrogen chloride, and then kept for six hours. It has b. p. 93—96°/8—9 mm. and m. p. 63°. With alcoholic potassium hydroxide it yields *nor*dicyclo*eksantalane*, b.p. 62—64°/9 mm. or 186—189°/760 mm., D^{20} 0·8827, n_D 1·4779, and α_D −19°. The same hydrocarbon appears to be formed when *tricyclo*santalic acid is heated with concentrated hydrochloric acid at 180°. *tricyclo*Eksantalic acid, when treated with 50% sulphuric acid, yields the dicyclic acid together with a *lactone*, $C_{11}H_{16}O_2$, b. p. 153—154°/10 mm., and m. p. 102°.

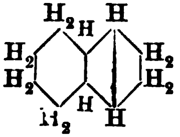
When santalol is heated with alcoholic potassium hydroxide at 160° for two hours the molecule is ruptured at the double bond in the side-chain and the tricyclic system is converted into a dicyclic, the resulting product being *dicyclo*eksantalol. When *tricyclo*santalol is treated with a methyl alcoholic solution of hydrogen chloride the product appears to be an O-*methyl* ether, b. p. 145—160°/10 mm., D^{20} 0·958, n_D 1·496, and α_D −30°. A dicyclo*santalol* is formed when *tricyclo*santalol is warmed at about 45° with acetic acid and a little concentrated sulphuric acid, it has b. p. 155—175°/10 mm., D^{20} 0·981, n_D 1·5179, and α_D −28°.

When the methyl ester of hydrochloro*dicyclo*eksantalic acid is reduced with sodium and alcohol, *dihydro*dicyclo*eksantalic acid*, $C_{11}H_{18}O_2$, b. p. 166—169°/10 mm. and m. p. 58°, is obtained. The corresponding *methyl* ester has b. p. 127—132°/9 mm., D^{20} 1·009, and n_D 1·48131. *Dihydro*dicyclo*eksantalol*, $C_{11}H_{20}O$, obtained by reducing the ester, has b. p. 128—133°/10 mm., D^{20} 0·9724, and n_D 1·492.

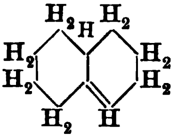
J. J. S.

Constituents of Essential Oils. Friedrich W. Semmler (*Ber.*, 1907, 40, 1120—1124).—Attention is drawn to the need of exercising great care in applying molecular refraction data to the elucidation of the constitution of natural products. Dicyclic derivatives usually have a higher value than the theoretical. Santalol and its derivatives probably contain a tricyclic system. Santalol itself, $C_{15}H_{24}O$, contains a side-chain of 5-carbon atoms, including a double valency and a primary alcoholic group. When oxidised it yields tricyclic eksantalic acid, $C_{11}H_{16}O_2$, from which a hydrocarbon, $C_{10}H_{16}$, can be obtained by the elimination of carbon dioxide. The molecular increments of these compounds are somewhat less than those required for a dicyclic system with a double valency. When heated with mineral acids they are converted into isomeric compounds the increments of which correspond exactly with those required for a dicyclic system with a double valency. Hence the original compounds presumably contained a tricyclic system.

The formulæ suggested for the two hydrocarbons, $C_{10}H_{16}$, are

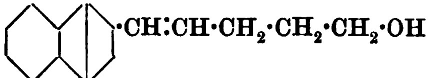


Nor*tricyclo*eksantalan.

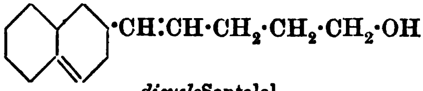


Nor*dicyclo*eksantalan.

and similarly for the santalols,



*tricyclo*Santalol.

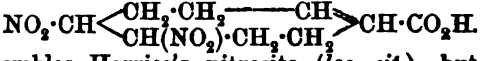


*dicyclo*Santalol.

as the boiling points and sp. gr. of nor*dicyclo*eksantalan are identical with those of octahydronaphthalene, although, so far, it has not been possible to obtain naphthalene or any of its derivatives from the hydrocarbon $C_{10}H_{16}$.

J. J. S.

Caoutchouc Nitrosite and its Use for the Analysis of Crude Caoutchoucs and Caoutchouc Products. Paul Alexander (*Ber.*, 1907, 40, 1070—1078. Compare Abstr., 1905, i, 223).—The product obtained by the action of nitrous fumes (prepared from starch and nitric acid, D 1·4) on caoutchouc has the composition C 44·92, H 5·37, N 11·67, independently of the source, agreeing with the formula $C_9H_{12}O_6N_2$, and not identical with Harries's nitrosite, $C_{10}H_{15}O_7N_3$ (Abstr., 1905, i, 223). The same compound was obtained previously by the action of the nitrous decomposition products of lead nitrate (*loc. cit.*). This is the first C_9 derivative of caoutchouc, and, on the basis of Harries's dimethyl*cyclo*octadiene caoutchouc formula, a carbon atom must have been eliminated during the reaction. This was identified as carbon dioxide; probably the methyl groups of caoutchouc are oxidised to carboxyl which is eliminated from that carbon to which both nitro-and carboxyl groups are attached, forming 5 : 6-*dinitro-cyclooctene-1-carboxylic acid*,



$$NO_2\cdot CH\left<\begin{array}{l}CH_2\cdot CH_2\text{———}CH\\CH(NO_2)\cdot CH_2\cdot CH_2\end{array}\right>CH\cdot CO_2H.$$

This nitrosate closely resembles Harries's nitrosite (*loc. cit.*), but decomposes at 90—110°.

One gram of caoutchouc, purified by exhaustive extraction with acetone, yields about 2·1 grams of nitrosate, whereas 1 gram of vulcanised caoutchouc gives rise to 2·4 grams of sulphur free nitrosate.

The observations made with caoutchoucs of different origin show them all to contain a hydrocarbon, $C_{10}H_{16}$, but that the extent to which this is polymerised probably varies with different natural products.

An additive product of caoutchouc with picric acid could not be prepared. E. F. A.

Albans from Ficus Vogelii. DAVID SPENCE (*Ber.*, 1907, **40**, 999—1000).—The genetic relationship of the sugar-like substances to caoutchouc and the gums having been suggested by Tschirch, it seemed probable that intermediate substances might be found in the resins. From this point of view the author has investigated the resin obtained by extraction of the caoutchouc of *Ficus Vogelii* with boiling acetone. On repeated recrystallisation of the resin from absolute alcohol, two isomeric *substances*, $C_{16}H_{26}O$, m. p. 201—205° and 154°, are obtained. These are neutral to acids or alkalis and are not attacked by alcoholic potassium hydroxide. In agreement with Tschirch's nomenclature (Abstr., 1905, i, 452), the names α- and β-alban are suggested. G. Y.

Linamarin, the Cyanogenetic Glucoside of Flax. ARMAND JORISSEN (*Bull. Acad. roy. Belg.*, 1907, 12—17. Compare Jorissen, Abstr., 1885, 181, with Hairs, Abstr., 1892, 502; Dunstan and Henry, Abstr., 1904, ii, 71, and with Auld, Abstr., 1906, ii, 794).—Dunstan, Henry, and Auld (*loc. cit.*) have shown that the cyanogenetic glucoside (phaseolunatin) contained in the beans of *Phaseolus lunatus* is identical with the linamarin which Jorissen and Hairs isolated from the embryo flax plants, and have suggested that the name linamarin should be superseded by phaseolunatin. The author claims that as the flax glucoside was isolated and described by him sixteen years ago the name linamarin should be adhered to. Attention is also directed to Kohn-Abrest's statement (Abstr., 1906, ii, 625) that the beans of *Phaseolus lunatus* contain more than one cyanogenetic glucoside (see, however, Dunstan and Henry, *Ann. Chim. Phys.*, 1907, [viii], **10**, 118). T. A. H.

Natural Colouring Matters. LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1907, 3, 287—306).—1. *Bixin* [with LADISLAUS MATEJKO] (compare Abstr., 1906, i, 760). 2. *Constituents of the Root of Datisca Cannabina* [with A. KORCZYŃSKI] (compare Schunck and Marchlewski, Abstr., 1904, i, 142, 340).—Datiscetin has the composition $C_{15}H_{10}O_6$, and after repeated crystallisation from glacial acetic acid has m. p. 268—269°. It contains no methoxy-groups, does not reduce Fehling's solution, but readily reduces an ammoniacal solution of silver nitrate. A *tetra-acetyl* derivative, $C_{15}H_6O_6Ac_4$, is readily obtained by Liebermann's method. It crystallises from ether in colourless needles, m. p. 138°. The *tetrabenzoyl* derivative, obtained by the action of benzoyl chloride in the presence of pyridine, crystallises from dilute acetone in colourless needles, m. p. 190—191°. The *tetrabenzenesulphonyl* derivative, $C_{15}H_6O_6(SO_2Ph)_4$, crystallises from glacial acetic acid in needles, m. p. 188°. When the glucoside datiscin is hydrolysed with dilute sulphuric acid, datiscetin and dextrose (not rhamnose) are formed. The formula $C_{21}H_{20}O_{11},H_2O$ is suggested for the glucoside.

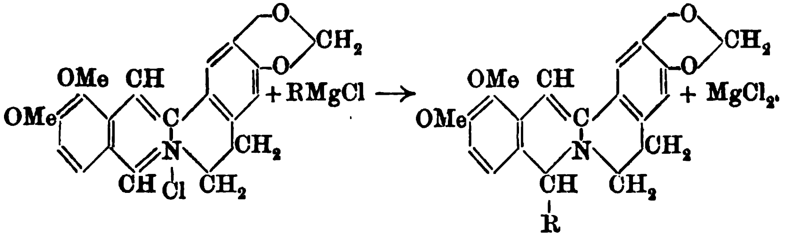
3. *Chlorophyll* [with P. KOŹNIEWSKI] (compare Willstätter, this vol., i, 69, 71).—Chlorophyll which has been completely freed from *allo*chlorophyll and lipochrome yields phyllocyanin and phylloxanthin when its ethereal solution is shaken with concentrated hydrochloric acid, and hence both compounds are probably derived from the same substance. Phylloxanthin is not transformed into phyllocyanin when kept in contact with hydrochloric acid at the ordinary temperature.

J. J. S.

Kamala and Rottlerin. HANS TELLE (*Arch. Pharm.*, 1907, 245, 69—70).—A claim of priority against Thoms (*ibid.*, 244, 644) (compare Abstr., 1906, i, 973).

C. F. B.

Preparation of Berberine Derivatives. EMANUEL MERCK (D.R.-P. 179212).—The salts of berberine, when treated with the Grignard reagent, interact to form alkyldihydroberberines in accordance with the following diagram:



Benzyldihydroberberine, m. p. 161—162°, obtained from berberine chloride or cyanide by the action of magnesium benzyl chloride, crystallises in small, rhombic plates; *hydrochloride*, m. p. 165—166°. *Phenyldihydroberberine*, m. p. 194—195°, forms brownish-yellow plates with pointed ends. *Methyldihydroberberine*, yellow crystals, m. p. 134°, was prepared from berberine chloride and magnesium methiodide; *hydriodide*, pale yellow leaflets, m. p. 249°. The following bases were similarly obtained: *ethyl dihydroberberine*, leaflets, m. p. 164—165°; *hydriodide* decomposes at 223°; *propyldihydroberberine*, leaflets, m. p. 132°, hydriodide decomposing at 207°. G. T. M.

Carnosine and Ignotine. WLADIMIR VON GULEWITSCH (*Zeitsch. physiol. Chem.*, 1907, 51, 258—260. Compare Abstr., 1900, i, 516; this vol., i, 264)—Polemical, a reply to Kutscher (this vol. i, 337). W. D. H.

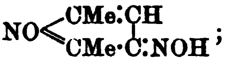
Solubility and Melting Point of Morphine. EDWARD J. GUILD (*Pharm. J.*, 1907, [iv], 24, 357).—Many of the values recorded for the solubility of morphine are much too high, probably on account of the presence of traces of codeine in the samples tested. Determinations of the solubility of a specimen of morphine, which had been crystallised from alcohol and subsequently washed with alcohol and ether, showed that the hydrated alkaloid, $C_{17}H_{19}O_3N,H_2O$, is soluble in water to the extent of about 1 in 5200. The electrical conductivity of the solution is considerably greater than that of pure water. The m. p. of morphine is of no value as a test of purity. The anhydrous alkaloid gradually darkens above 225° and melts to a dark brown tar at 245—250°; this decomposition is not attended by any loss in weight. E. G.

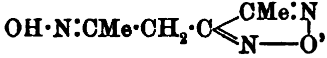
Brucine Oxide. AMÉ PICTET and G. JENNY (*Ber.*, 1907, 40, 1172—1175).—*Brucine oxide*, $C_{23}H_{26}O_5N_2,4\frac{1}{2}H_2O$, m. p. 124—125° (anhydrous, 199° decomp.), obtained in a similar manner to strychnine oxide (Abstr., 1905, i, 816), forms large, colourless, rhombic prisms [$a:b:c=0.54673:1:0.44734$]. The aqueous solution has a neutral reaction, an intensely bitter taste, and $[\alpha]_D^{28}-1.63°$. The colour reactions of the oxide are like those of brucine itself. In the crude state the oxide develops a blue coloration in starch potassium iodide solution, but loses this property after repeated crystallisation from water; the same is true of strychnine oxide. The physiological action of brucine oxide is less pronounced than that of the alkaloid.

The oxide, which is reconverted into brucine by sulphurous acid, behaves as a monoacid base; the salts are lævorotatory in aqueous solution and are changed by sulphurous acid into the salts of brucine. The *hydrochloride*, $C_{23}H_{26}O_5N_2,HCl,H_2O$, m. p. >300°, $[\alpha]_D^{28}-13.95°$; *platinichloride*, $(C_{23}H_{26}O_5N_2)_2,H_2PtCl_6$; *nitrate*, $C_{23}H_{26}O_5N_2,HNO_3,H_2O$, $[\alpha]_D^{30}-11.36°$; *hydrogen sulphate*, and the *picrate* are mentioned. C. S.

Researches on the Hydroxypyrroles. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 271—275. Compare Abstr., 1904, i, 526; this vol., i, 153).—In continuation of the study of the action of nitrous acid on indoles and pyrroles (*loc. cit.*), the authors are investigating the behaviour towards this acid of derivatives in which the iminic hydrogen is replaced by hydroxyl. The present paper contains an account of the results obtained with 1-hydroxy-2:5-dimethylpyrrole.

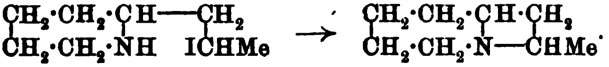
3-*Nitroso*-1-*hydroxy*-2:5-*dimethylpyrrole*, obtained by the action of sodium ethoxide and amyl nitrite on 1-hydroxy-2:5-dimethylpyrrole, exhibits behaviour best explained by the tautomeric structure


$\mathrm{NO}<\begin{array}{l}\mathrm{CMe{:}CH}\\ \mathrm{CMe{\cdot}C{:}NOH}\end{array}$; it crystallises from ether in long, orange-coloured needles which begin to decompose without melting at about 80° and dissolves readily in alcohol or water and sparingly in benzene. This compound is characterised by the ease with which it undergoes hydrolysis accompanied by opening of the ring; different hydrolytic reagents yield various products, which are, however, all simply related to the original substance. In every case the final product of hydrolysis is the dioxime of a trione, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(N{\cdot}OH){\cdot}CMe(N{\cdot}OH)$, which could not be isolated.

In presence of hydroxylamine, however, the corresponding trioxime, $OH{\cdot}N{:}CMe{\cdot}C(N{\cdot}OH){\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH$ (compare Angeli, Angelico, and Calvello, Abstr., 1904, i, 188, 447), is obtained. This trioxime readily loses water, yielding the *anhydride*,  $\mathrm{OH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}C}<\begin{array}{l}\mathrm{CMe{:}N}\\ \mathrm{N{-}{-}O}\end{array}$, which crystallises from water in colourless needles, m. p. 83°, and gives a *benzoyl* derivative, $C_6H_8O_2N_3Bz$, crystallising from a mixture of benzene and light petroleum in needles, m. p. 106°.

3-Nitroso-1-hydroxy-2 : 5-dimethylpyrrole yields a *benzoyl* derivative, $C_{20}H_{18}O_5N_2$, which crystallises from alcohol in shining, colourless plates, m. p. 169°. When boiled with 25% sulphuric acid, the sodium derivative of the nitrous compound is converted into the compound $C_6H_8O_2N_2$, m. p. 117° (compare Angelico and Calvello, Abstr., 1904, i, 447). T. H. P.

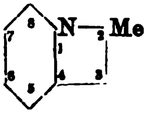
2-Ethylconidine and some Piperidine Bases. KARL LÖFFLER and PHILLIP PLÖCKER (*Ber.*, 1907, 40, 1310—1324).—It has previously been shown that 2-β-iodopropylpiperidine, when warmed with sodium hydroxide, forms a saturated, dicyclic, tertiary base, thus:


$$\begin{array}{l}\mathrm{CH_2{\cdot}CH_2{\cdot}CH{-}{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}NH\quad ICHMe}\end{array}\longrightarrow\begin{array}{l}\mathrm{CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}N{-}{-}CHMe}\end{array}.$$

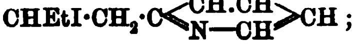
The latter base resembles Hofmann's "ε-coniceine," prepared from the iodoconiine, obtained by heating conhydrine with fuming hydriodic acid, Hofmann's base being, however, optically active. It is accordingly suggested that conhydrine and 2-β-iodopropylpiperidine are identical in structure.

It is shown that dicyclic compounds, containing both a 4- and a 6-ring, may also be obtained from 2-β-hydroxybutylpiperidine and 2-ω-hydroxy*iso*propylpiperidine respectively.

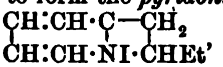
With regard to the nomenclature of this new type of compound, the base, obtained from 2-β-hydroxypropylpyridine, is termed 2-methylconidine (see annexed scheme).



2-β-Hydroxybutylpyridine, obtained by heating α-picoline, water, and propaldehyde for eighteen to twenty hours at 160—170°, has b. p. 124—126°/14 mm. (Matzdorff gives b. p. 125—127°/18 mm.). When heated with fuming hydriodic acid it forms 2-β-iodobutylpyridine,

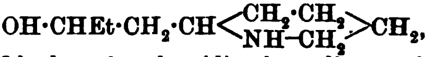
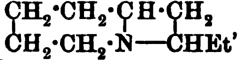

$$\mathrm{CHEtI{\cdot}CH_2{\cdot}C}<\begin{array}{l}\mathrm{CH{:}CH}\\ \mathrm{N{-}CH}\end{array}>\mathrm{CH};$$

it forms a yellow oil which in alcoholic solution undergoes intramolecular rearrangement to form the *pyridonium iodide*,



$$\begin{array}{l} \mathrm{CH{:}CH{\cdot}C{-}CH_2} \\ \mathrm{CH{:}CH{\cdot}NI{\cdot}CHEt} \end{array}$$

m. p. 153—154°.

2-*β*-*Hydroxybutylpiperidine*,  $\mathrm{OH{\cdot}CHEt{\cdot}CH_2{\cdot}CH}\!<\!\begin{array}{l}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{NH{-}CH_2}\end{array}\!>\!\mathrm{CH_2}$, obtained by the reduction of 2-*β*-hydroxybutylpyridine by sodium and ethyl alcohol, boils at 125—130°/15 mm., and has m. p. 46—55°. Since two racemic forms are possible, owing to the reduction, the product probably contains a little of the stereoisomeride. It was converted into its iodide by heating with fuming hydriodic acid and red phosphorus for eight hours at 140°; the crude iodide, obtained as an oil, was then heated with concentrated aqueous potassium hydroxide (1 : 1), when 2-*ethylconidine*,  $\begin{array}{l}\mathrm{CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}N{-}CHEt}\end{array}$, was obtained; the latter was purified by crystallisation of its picrate (m. p. 198°); it has b. p. 176—183° and D_4^{15} 0·8991; it is possibly mixed with a diastereoisomeride. The *aurichloride* has m. p. 132—135°; the *platinichloride* has m. p. 205—210 (decomp.); the *mercurichloride* separates in prisms, m. p. 220—221°; the *ethiodide* has m. p. 222° (decomp.).

2-*β*-Hydroxybutylpyridine, obtained by the condensation of *n*-propaldehyde with *a*-picoline, was heated with concentrated sulphuric acid and glacial acetic acid for six hours at 160—165°; a product was obtained, b. p. 190—210°, containing butenylpyridine, which was identified by means of its platinichloride, m. p. 140—150° (decomp.) (Matzdorff gives 140°); the *aurichloride* has m. p. 154—156° (decomp.); the *picrate* has m. p. 154°, and the *mercurichloride*, m. p. 93—94°. The yield of butenylpyridine was small.

2-*β*-Hydroxybutylpyridine was converted into 2-butylpyridine, according to Willstätter's method, the hydroxy-group being first replaced by iodine and the resulting iodide then reduced by zinc dust in acid solution. *a-Butylpyridine picrate* has m. p. 94° and serves for the purification of the free *base*, $C_9H_{13}N$, which is a transparent oil with b. p. 189—192° and D_4^{15} 0·9135; the *aurichloride* has m. p. 85°; the *platinichloride*, m. p. 144—145°, and the *mercurichloride*, m. p. 102°.

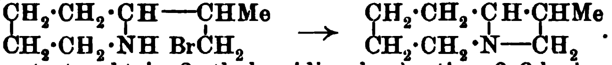
When 2-*β*-hydroxybutylpyridine was heated in a bomb-tube with fuming hydrobromic acid and red phosphorus for eight hours at 130—140°, 2-*β*-bromobutylpyridine was obtained; it undergoes molecular rearrangement into the pyridonium bromide, m. p. 135—140°, a syrup, which was identified by its conversion into the pyridonium chloride (*supra*) by agitating it with freshly-precipitated silver chloride.

When the product of the bromination of 2-*β*-hydroxybutylpyridine was reduced by zinc dust and hydrochloric acid, 2-butylpyridine was not obtained, but a *base* with b. p. 197°, and unsaturated, since it reduces permanganate; it forms a *platinichloride*, $(C_9H_{11}N,HCl)_2PtCl_4$, with m. p. 162—163° (decomp.); a *picrate* with m. p. 153°; an *aurichloride* with m. p. 130°, and a *mercurichloride* with m. p. 120—130°. The substance is not identical with butenylpyridine.

2-*Butylpiperidine*, $C_{19}H_{19}N$, obtained by the reduction of 2-butylpyridine with sodium and ethyl alcohol, is a transparent, mobile liquid with b. p. 186—189° and D_4^{15} 0·8529. It has an odour resembling that of coniine. Its *hydrochloride* has m. p. 181—182° and its *platinichloride*, m. p. 137—140°.

Attempts were made to resolve 2-butylpiperidine into its optically active components. When the *dl*-base was neutralised by *d*-tartaric acid, the crop obtained yielded a base with a_D + 6·537° ($l = 1$) and D 0·8512. On further treatment of this product, a base having a_D + 13·41° ($l = 1$) was obtained, but the purification of the *d*-base was not further effected. A platinichloride was obtained, having m. p. 131—132°. A lævorotatory base, having a_D – 15·96° ($l = 1$) and D 0·8533, was obtained by decomposing the mother liquor from the previous crystallisation of the *d*-base *d*-tartrate and neutralising the lævorotatory product with *l*-tartaric acid. A. McK.

3-Methylconidine and some Pyridine Bases. Karl Löffler and Alfred Grosse (*Ber.*, 1907, **40**, 1325—1336. Compare preceding abstract).—2-ω-Hydroxy*iso*propylpiperidine may be converted into 3-methylconidine, thus:



Attempts to obtain 2-ethylpyridine by heating 2-β-hydroxyethylpyridine with concentrated hydrochloric acid and glacial acetic acid in order to form α-vinylpyridine, which could then be reduced, were unsuccessful. 2-Ethylpyridine was obtained by heating 2-β-hydroxyethylpyridine with fuming hydrobromic acid and phosphorus in a bomb-tube at 135° for ten to twelve hours and then reducing by zinc dust and acid, according to Willstätter's method.

When formaldehyde acts on 2-ethylpyridine, three reactions take place: (1) 2-ω-hydroxy*iso*propylpyridine is formed, thus:

$$C_5H_4N{\cdot}CH_2Me + CH_2O = C_5H_4N{\cdot}CHMe{\cdot}CH_2{\cdot}OH;$$

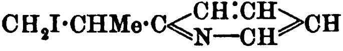
(2) 2-di-ω-hydroxy-*tert*.-butylpyridine is formed, thus:

$$C_5H_4N{\cdot}CH_2Me + 2CH_2O = C_5H_4N{\cdot}CMe(CH_2{\cdot}OH)_2;$$

(3) 2-α-methylvinylpyridine is formed by the elimination of water from 2-ω-hydroxy*iso*propylpyridine, thus: $C_5H_4N{\cdot}CHMe{\cdot}CH_2{\cdot}OH = H_2O + C_5H_4N{\cdot}CMe{:}CH_2$.

2-*Di-ω-hydroxy*-tert.-*butylpyridine* has b. p. 168—171°/13 mm.; its *picrate* has m. p. 116—117°; its *aurichloride*, m. p. 125—126°, and its *platinichloride*, m. p. 153—155°.

2-α-*Methylvinylpyridine* has b. p. 170—173°, has an odour reminiscent of 2-vinylpyridine, is unsaturated, has D^{15} 0·9706; its *aurichloride* has m. p. 135°; its *platinichloride*, m. p. 163—164°, and its *picrate*, m. p. 148—149°. When reduced by alcohol and sodium, it is converted into Ladenburg's *iso*propylpiperidine.



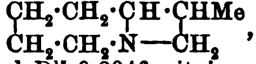
2-ω-*Iodo*iso*propylpyridine*, $CH_2I{\cdot}CHMe{\cdot}C{<}\begin{matrix}CH{:}CH\\N{-}CH\end{matrix}{>}CH$, obtained by heating 2-ω-hydroxy*iso*propylpyridine in a bomb-tube for ten hours at 130—135° with fuming hydriodic acid and red phosphorus, is an oil which was characterised by its *platinichloride*, m. p. 142—145° (decomp.), and its *picrate*, m. p. 87—89°. Its transformation into the corresponding pyridonium iodide takes place with greater difficulty than is the case with the iodides of 2-β-hydroxyethylpyridine, 2-β-hydroxypropylpyridine, and 2-β-hydroxybutylpyridine respectively, heating for seven to eight hours at 140—150° being necessary.

In the hope of obtaining 2-*tert.*-butylpyridine, 2-di-ω-hydroxy-*tert.*-butylpyridine was heated with hydriodic acid, when, however, only one hydroxyl group was replaced by iodine; the *platinichloride*, $C_5H_4N\cdot CMe(CH_2I)\cdot CH_2\cdot OH,H_2PtCl_6$, has m. p. 153—155° (decomp.); the corresponding *aurichloride* has m. p. 89—90°.

2-ω-Hydroxy*iso*propylpiperidine, obtained by the reduction of 2-ω-hydroxy*iso*propylpyridine, forms an *aurichloride*,

$$C_8H_{17}ON,HCl,AuCl_3,$$

which has m. p. 105—106°. 2-ω-Hydroxy*iso*propylpiperidine was heated in a bomb-tube for ten hours at 130—135° with concentrated hydrobromic acid and red phosphorus. The resulting bromide, when acted on by potassium hydroxide, formed 3-*methylconidine*,



$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot CHMe \\ CH_2\cdot CH_2\cdot N\text{—}CH_2 \end{array},$$

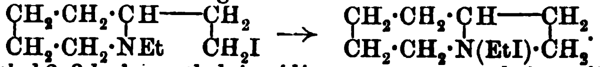
which has b. p. 158° and D_4^{15} 0·8946; it is a colourless liquid with a disagreeable odour and is very poisonous; its *picrate* has m. p. 194—195° and serves for the purification of the base itself; its *platinichloride* has m. p. 197—199°; its aurichloride has m. p. 150—151°, and its *mercurichloride* has m. p. 205—206°; its *ethiodide* has m. p. 169° and forms a *platinichloride*, m. p. 185—187°.

3-Methylconidine has two asymmetric carbon atoms and may accordingly exist in two racemic forms. The constancy of the boiling point of the product obtained and the sharp melting points of its salts indicate that one of these forms, if present at all, can only be present in traces. The more sparingly soluble salt, obtained by resolving the *dl*-base with *d*-tartaric acid, gave a base having $[\alpha]_D^{17}$ $-17\cdot13°$; the base obtained from the mother liquor was converted into a salt by means of *l*-tartaric acid, when a base having $[\alpha]_D^{8}$ $+16\cdot0°$ was obtained.

A. McK.

An Attempt to Synthesise Conidine. KARL LÖFFLER and ALFRED GROSSE (*Ber.*, 1907, **40**, 1336—1342. Compare preceding abstracts).—The authors describe an unsuccessful attempt to synthesise conidine.

When Ladenburg's 1-ethyl-2-β-hydroxyethylpiperidine was treated with hydriodic acid, it was expected that the resulting iodo-compound might be made to undergo transformation into conidine ethiodide, thus:



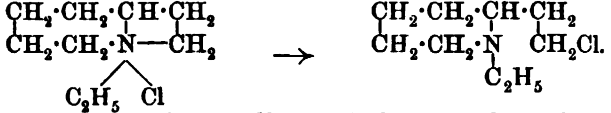
$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\text{——}CH_2 \\ CH_2\cdot CH_2\cdot NEt \quad CH_2I \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CH_2\cdot CH\text{——}CH_2 \\ CH_2\cdot CH_2\cdot N(EtI)\cdot CH_2 \end{array}.$$

1-*Ethyl*-2-β-*hydroxyethylpiperidine* was converted into its *bromo*-derivative by heating for ten hours at 130° in a bomb-tube with fuming hydrobromic acid and phosphorus; it separates from acetone in crystalline nodules, m. p. 172°.

1-*Ethyl*-2-*hydroxyethylpiperidine platinichloride* has m. p. 165—166°.

The 1-*ethyl*-2-β-*bromoethylpiperidine* separates from alcohol in felted needles, m. p. 165—166°. Conidine ethiodide was precipitated as a white powder by the action of alkali on the preceding compound, but owing to its hygroscopic nature was not analysed. When agitated with freshly-precipitated silver chloride, it was converted into conidine ethochloride, from which the *platinichloride*, $(C_9H_{18}NCl)_2PtCl_4$, was obtained, m. p. 178° (decomp.).

When the ethochloride is heated at 170°, ethyl chloride is not eliminated, but the four-membered ring is broken with the formation of 1-*ethyl-2-β-chloroethylpiperidine*, thus:



The latter compound has D^{15} 0·9964, forms a *platinichloride* with m. p. 168—170°, and an *aurichloride* with m. p. 109—110°.

When 1-ethyl-2-β-chloroethylpiperidine is allowed to remain at the ordinary temperature for a long time, an oil separates, the four-membered ring is again closed, the chlorine atom attaching itself to nitrogen; the *platinichloride*, $(C_9H_{18}NCl)_2,PtCl_4$, obtained from this product has, however, the m. p. 192—193° and not 178° as might have been expected. The latter curious observation may be due to dimorphism or may be interpreted in the light of Ladenburg's theory of tervalent asymmetric nitrogen. A. McK.

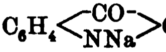
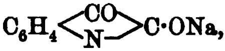
Resolution of Phenyl-α-picolylalkine [2-β-Hydroxy-β-phenylethylpyridine] into its Optically-active Components. Karl Löffler and Herbert Grunert (*Ber.*, 1907, 40, 1342—1347).—2-β-Hydroxy-β-phenylethylpyridine was first obtained by Roth (Abstr., 1907, i, 165) by heating benzaldehyde, α-picoline, and water in a sealed tube at 135°. The modification of this method, as described by Bach (*ibid.*, 610), who conducted the heating at 160°, was found unsuitable by the authors, who obtained stilbazole as the main product at this temperature. Several of the data given by Roth and Bach are inaccurate.

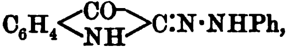
2-β-Hydroxy-β-phenylethylpyridine, obtained by Roth's method, separates from water in glistening leaflets, m. p. 107—108° (Roth gives 96—97°). The platinichloride has m. p. 174—175° (Roth gives 170—172°); the aurichloride has m. p. 141—142° (Roth gives 131—132°); the *hydrobromide* separates from water in silky needles, m. p. 80—81°; the *picrate* has m. p. 123—124°.

An attempt to resolve 2-β-hydroxy-β-phenylethylpyridine into its optically active components by means of *d*-tartaric acid failed, the hydrogen *d*-tartrate obtained apparently being partially racemic. The base was resolved by means of Reychler's *d*-camphorsulphonic acid. 1-2-*β-Hydroxy-β-phenylethylpyridine*, obtained from the more sparingly soluble camphorsulphonate, has $[\alpha]_D^{25}$ −36·44° in chloroform solution and m. p. 128—129°. Its *platinichloride* has m. p. 163° and its *aurichloride*, m. p. 138°.

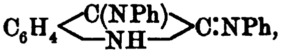
The preparation of the pure *d*-base was not successful.

This is the first case of the resolution of an alkine into its optical antipodes. A. McK.

Colour Phenomena in Alkaline Isatin Solutions. GUSTAV HELLER [and, in part, OTTO NÖTZEL] (*Ber.*, 1907, 40, 1291—1300. Compare Heller and Mayer, Abstr., 1906, i, 585; Peters, this vol., i, 239, and following abstract).—The constitutions of the metallic derivatives of isatin and the causes underlying the changes of colour observed in alkaline solutions of isatin are discussed. Sodioisatin, formed by the action of sodium ethoxide on isatin, is considered to be an *N*-derivative,  $C_6H_4<\begin{smallmatrix}CO-\\NNa\end{smallmatrix}>CO$, as it yields *N*-benzoylisatin with benzoyl chloride at the laboratory temperature, and *N*-methyl- and *N*-ethyl-isatins with methyl and ethyl iodides respectively at 100°. When dissolved in water, this sodium derivative undergoes the same changes of colour as are observed on dissolving isatin in an aqueous alkali, the solution which is at first violet-red gradually becoming yellow. This change, which is accelerated by heat and by addition of an excess of the alkali, results in the formation of sodium isatoate; it is probable that the *O*-sodium derivative,  $C_6H_4<\begin{smallmatrix}CO\\N\end{smallmatrix}>C\cdot ONa$, is formed as an intermediate product of the change. Conversely, sodium isatoate is converted into isatin by the action of hydrochloric acid.

When treated with aqueous silver nitrate, *N*-sodium isatin yields the *O*-silver derivative, which with methyl iodide forms *O*-methylisatin (von Baeyer and Oeconomides, Abstr., 1883, 201). This reacts readily at the ordinary temperature with aniline, forming α-isatinanilide (Sandmeyer, Abstr., 1903, i, 486), which with an excess of aniline forms the dianil readily at the moment of its formation, but after isolation only when heated with aniline. With phenylhydrazine, *O*-methylisatin forms isatinphenylhydrazone,  $C_6H_4<\begin{smallmatrix}CO\\NH\end{smallmatrix}>C{:}N\cdot NHPh$, which is formed also by the action of the hydrazine on α-isatinanilide and is identical with benzeneazoindoxyl (von Baeyer, Abstr., 1884, 74).

When heated with iodine and ether at 100°, *N*-sodium isatin yields an unstable, blue *compound*, which is decomposed by hot water, forming isatin and iodine.

Isatindianil,  $C_6H_4<\begin{smallmatrix}C(NPh)\\NH\end{smallmatrix}>C{:}NPh$, crystallises from benzene in dark red prisms, m. p. 210°, is stable towards alkalis, but is hydrolysed by hydrochloric acid, forming isatin, and is decolorised by reducing agents, becoming again red on exposure to air.

The action of methyl iodide on silver isatoate leads to the formation of isatin and *N*-methylisatin. G. Y.

Conductivity of *N*-Sodioisatin and Sodium Isatoate in Aqueous Solution. ERNST DEUSSEN, GUSTAV HELLER, and OTTO NÖTZEL (*Ber.*, 1907, 40, 1300—1303. Compare preceding abstract).—The change of *N*-sodioisatin in aqueous solution into sodium isatoate, and the conversion of sodium isatoate into isatin and sodium chloride by the action of hydrochloric acid are accompanied by corresponding changes in the conductivities of the solutions. The conductivity measurements were carried out at 25°.

Three minutes after formation, a 0·5% solution of *N*-sodium isatin has the specific conductivity $\kappa.10^2 = 0{\cdot}244$, and after 230 minutes, $\kappa.10^2 = 0{\cdot}209$; this final specific conductivity is identical with that of a solution of sodium isatoate of corresponding strength. The curve representing the change does not permit of any conclusion as to the intermediate formation of *O*-sodium isatin. Sodium isatoate has the molecular conductivity $\mu = 64{\cdot}1$, $68{\cdot}4$, $71{\cdot}1$, and $77{\cdot}5$, with $v = 10$, 20, 40, and 80 respectively. These values are compared with those obtained for sodium *o*-aminobenzoate: $\mu = 66{\cdot}5$, $68{\cdot}0$, and $71{\cdot}4$, with $v = 32$, 64, and 128 respectively.

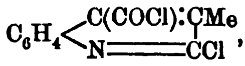
On addition of 5 c.c. *N*/10 hydrochloric acid to a solution of 0·0935 gram of sodium isatoate in 20 c.c. of water, the yellow solution gradually becomes red and after some time isatin commences to separate. After two minutes the solution has the conductivity $\kappa.10^2 = 0{\cdot}630$, and, after twenty-eight and a quarter hours, $\kappa.10^2 = 0{\cdot}287$. From this the specific conductivity of isatoic acid is calculated as $\kappa.10^2 = 0{\cdot}41$ with $v = 50$, and its degree of dissociation as $a = \mu_v/\mu_\infty = 0{\cdot}54$.

G. Y.

Preparation and Properties of 3-Methylcinchonic and 2-Hydroxy-3-methylcinchonic Acids. G. Ornstein (*Ber.*, 1907, **40**, 1088—1095).—As both of these acids contain a methyl group and a benzene nucleus contiguous to the carboxyl group, it was expected that they would conform to V. Meyer's esterification rule, and the author's experiments confirm this.

3-Methylcinchonic acid was obtained by heating isatin, propaldoxime, and potassium hydroxide for twelve to sixteen hours on the water-bath (von Miller, Abstr., 1890, i, 325). Its *hydrochloride* crystallises in needles, m. p. 240—241°; the *picrate* in yellow needles, m. p. 222—223°; the *platinichloride* is a yellow powder, and the *sodium* and *silver* salts are white powders. On heating the silver salt it decomposes, giving 3-methylquinoline (Abstr., 1885, 1079). The esters are obtained by heating the silver salt and alkyl iodide in a sealed tube at 100—150° for five hours. The *ethyl* ester does not crystallise; its *picrate*, m. p. 175—176°, and its *platinichloride* m. p. 224—225°; the *methyl* ester is a white powder which does not react with ammonia. The *chloride*, $C_{11}H_8ONCl$, prepared by heating the acid with thionyl chloride in a closed tube at 100° for five hours, crystallises in white needles, and the *amide*, $C_{11}H_{10}ON_2$, obtained from its benzene solution and ammonia, forms white needles, m. p. 228—229°, stable towards 15% potassium hydroxide, but hydrolysed by nitrous acid. The *anilide*, $C_{17}H_{14}ON_2$, forms white flakes, m. p. 238—239°.

2-Hydroxy-3-methylcinchonic acid (Meyer, Abstr., 1906, i, 108) was obtained by fusing methylcinchonic acid and potassium hydroxide; the *sodium* and *silver* salts are white. *2-Chloro-3-methylcinchonic chloride*,



$C_6H_4{<}\begin{array}{l}C(COCl){:}CMe\\ N{=\!=\!=}CCl\end{array}$, m. p. 52°, crystallises in yellow, prismatic needles and yields *2-chloro-3-methylcinchonic acid*, $C_{11}H_8O_2NCl$, when heated with water. It forms small, white needles, m. p. 191—192°. When heated in a sealed tube at 120° with water, chlorine is removed and 2-hydroxy-3-methylcinchonic acid is regenerated. *2-Chloro-3-methylcinchonamide*, $C_{11}H_9ON_2Cl$, crystallises in white needles, m. p. 270—271°; the *anilide*, $C_{17}H_{13}ON_2Cl$, forms white flakes, m. p. 267—268°. *Methyl 2-chloro-3-methylcinchonate*,

$$C_{12}H_{10}O_2NCl,$$

prepared from the chloride, crystallises in white needles, m. p. 78—79°. *Methyl 2-methoxy-3-methylcinchonate*, $C_{13}H_{13}O_3N$, obtained by heating the chloride in a sealed tube at 100° for two hours, forms white needles, m. p. 184—185°. All experiments to hydrolyse these esters, or to prepare the free acid, were without result. Heating the 2-methoxy-ester at 180° with water resulted in replacement of the methoxyl group by hydroxyl, and the amide and anilide of 2-hydroxy-3-methylcinchonic acid could also be obtained by heating the corresponding derivatives of chloromethylcinchonic acid with water at 180°; the *amide*, $C_{11}H_{10}O_2N_2$, m. p. 353—354°; the *anilide*, $C_{17}H_{14}O_2N_2$, has m. p. 314—315°. 2-*Anilino-3-methylcinchonic anilide*, $C_{23}H_{19}ON_3$, prepared by heating the chloride and aniline at 200°, forms white crystals, m. p. 322—323°.

3-Methylcarbostyril, $C_{10}H_9ON$, obtained by heating silver hydroxymethylcinchonate in a current of carbon dioxide, crystallises from acetone in glistening needles, m. p. 234—235°, and 2-*chloro-3-methylquinoline*, $C_{10}H_8NCl$, obtained by heating the carbostyril with phosphorus pentachloride at 130—140°, forms crystals, m. p. 89—90°.

W. R.

Preparation of Chlorinated Amidines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 178299).—2 : 4 : 5-*Trichloro*-6-*nitroacetanilide*, m. p. 194°, obtained by nitrating 2 : 4 : 5-*trichloroacetanilide*, m. p. 186—187°, when reduced with iron and dilute acetic acid in the presence of toluene, yields *acetyl*-2 : 4 : 5-*trichloro-o-phenylenediamine*, m. p. 200°, and the more soluble 2 : 4 : 5-*trichlorophenylethenylamidine*, m. p. 285°. The product consists entirely of the latter substance when the mixture is heated either alone at 200—290° or with glacial acetic acid at 100°.

2 : 4 : 5-*Trichloro*-6-*nitroformanilide*, m. p. 164°, obtained from 2 : 4 : 5-*trichloroformanilide*, m. p. 172—173°, yields 2 : 4 : 5-*trichlorophenylmethenylamidine*, m. p. 303—304°, and *formyl*-2 : 4 : 5-*trichloro-o-phenylenediamine*, m. p. 306°; the latter base, on melting, changes into the former. 2 : 4 : 5-*Trichloro*-6-*nitroformomethylanilide*,

$$NO_2{\cdot}C_6HCl_3{\cdot}NMe{\cdot}COH,$$

m. p. 124—125°, yields on reduction 2 : 4 : 5-*trichlorophenylmethylmethenylamidine*, m. p. 159—160°, and *formyl*-2 : 4 : 5-*trichloromethyl-o-phenylenediamine* having the same melting point. 2 : 4 : 5-*Trichloro*-6-*nitroacetoethylanilide*, m. p. 87—89°, furnishes on reduction a mixture of diamine and amidine, which on heating with glacial acetic acid gives the *acetate*, m. p. 98—99°, of the amidine, and this substance on heating at 100° yields the free 2 : 4 : 5-*trichlorophenylethylethenylamidine*, m. p. 116—117°.

Tetrachloro-o-nitroacetanilide gives an *acetyl-o-diamine*, m. p. 223—224°, and *tetrachlorophenylethenylamidine*, m. p. 300°.

Tetrachloro-*o*-nitroacetoethylanilide furnishes an *acetyl-o-diamine*, m. p. 203—204°, and *tetrachlorophenylethylethenylamidine*, m. p. 149°.

Tetrachlorobenzylethenylamidine, m. p. 176—177°, and *acetyltetra-*

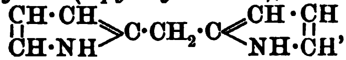
chlorobenzyl-o-*phenylenediamine*, m. p. 135—137°, are similarly produced from tetrachloro-*o*-nitroacetobenzylanilide.

Benzoyl-2 : 4 : 5-*trichloro*-o-*nitroaniline* on reduction gives *benzoyl*-2 : 4 : 5-*trichloro*-o-*phenylenediamine*, m. p. 205—207°, and this on distillation under reduced pressure furnishes 2 : 4 : 5-*trichlorobenzylbenzenylamidine*, m. p. 268—269°. G. T. M.

Action of Formaldehyde and of Methylene Chloride on Pyrrole. AMÉ PICTET and AUGUSTE RILLIET (*Ber.*, 1907, **40**, 1166—1172).—When pyrrole is shaken with a cold 40% formaldehyde solution a vigorous reaction ensues and a hard, insoluble, dark red compound is formed. When a few drops of sulphuric acid are added to a mixture of pyrrole and 4% formaldehyde solution, a condensation product, *formaldehyde-pyrrole*, $C_{11}H_{12}ON_2$, is formed, which is insoluble in all the ordinary solvents. In has no definite melting point, changes in colour to red on exposure to the air, and turns black when heated with concentrated hydrochloric acid. When subjected to destructive distillation, it yields as chief product 2-methylpyrrole, and thus the condensation appears to be of the same type as that observed by Dennstedt and Zimmermann (Abstr., 1886, 1043) in the case of paraldehyde and pyrrole. When the condensation product is distilled with zinc dust the chief product is α-picoline.

When potassium pyrrole and methylene chloride are heated for two hours at 120—130° (compare Ciamician and Dennstedt, Abstr., 1881, 826), a mixture of two condensation products is obtained which may be separated by means of their different solubilities in alcohol. 1 : 1-*Methylenedipyrrole*, $CH_2(C_4NH_4)_2$, crystallises from alcohol in colourless needles, m. p. 112°, is insoluble in cold water, acids, or alkalis, and does not yield a potassium derivative.

2 : 2-*Methylenedipyrrole* (*dipyridylmethane*),



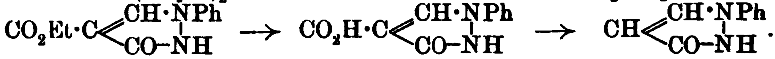
$$\begin{matrix}CH\cdot CH\\ \|\\ CH\cdot NH\end{matrix}\!>C\cdot CH_2\cdot C<\!\begin{matrix}CH\cdot CH\\ \|\\ NH\cdot CH\end{matrix},$$

is readily soluble in alcohol, but crystallises from light petroleum in colourless plates or broad needles, m. p. 66°. It reacts vigorously with potassium, yielding a colourless solid, insoluble in ether. The 1 : 1-derivative is converted into the isomeric 2 : 2-derivative when heated for four hours at 300°.

Both compounds have been distilled through hot tubes in the hope of obtaining 2-pyridyl-3-pyrrole, and thus arriving at a second synthesis of nicotine, but without success, pyridine itself being the only product of a pyridine-like nature which was isolated. J. J. S.

Preparation of 1-Phenyl-3-pyrazolone. AUGUST MICHAELIS and E. REMY (*Ber.*, 1907, **40**, 1020—1021).—The condensation of ethyl ethoxymethylenemalonate with acetylphenylhydrazine may be effected by means of phosphorus trichloride or oxychloride. By saponification of the product, 1-phenyl-3-pyrazolonecarboxylic acid, m. p. 216°, is obtained, which, when distilled, loses carbon dioxide with the formation of the 3-pyrazolone. The action is represented as follows:

$$OEt\cdot CH(CO_2Et)_2 + NHPh\cdot NH\cdot COMe = EtOH + CH_3\cdot CO_2Et +$$



$$CO_2Et\cdot C{<}\begin{array}{l}CH\cdot NPh\\ CO{-}NH\end{array} \rightarrow CO_2H\cdot C{<}\begin{array}{l}CH\cdot NPh\\ CO{-}NH\end{array} \rightarrow CH{<}\begin{array}{l}CH\cdot NPh\\ CO{-}NH\end{array}.$$

1-*Phenyl-3-pyrazolone*, $C_9H_8ON_2$, separates from alcohol in glistening leaflets, m. p. 155—156°, and is soluble in alkalis. A. McK.

Phosphorus Tribromide as a Reducing Agent (Conversion of Pyrazolones into Pyrazoles). RICHARD STOERMER and O. MARTINSEN (*Annalen*, 1907, **352**, 322—343. Compare Stoermer, Abstr., 1904, i, 181).—It was shown (*loc. cit.*) that when heated with phosphorus tribromide in a sealed tube at high temperatures a number of substances containing the group $\cdot CH_2\cdot CO\cdot$ or $\cdot NH\cdot CO\cdot$ are converted into the corresponding compounds containing the groups $\cdot CH{:}CH\cdot$ and $\cdot N{:}CH\cdot$ respectively. The work has been extended to establish the general nature of this reaction in the pyrazolone series. The results show that phosphorus tribromide is at least as good a reducing agent for such substances as phosphorus pentasulphide, and that cleaner products are obtained than when the latter is employed. The mechanism of the reduction of the pyrazolones cannot be that suggested previously in the case of the lactones, since no similar intramolecular transposition of alkyl groups takes place, but alkyl groups attached to the carbon atom in the α-position to the carbonyl are removed along with the oxygen. At low temperatures, bromopyrazoles are formed (compare Michaelis and Behn, Abstr., 1900, i, 693); as these are reduced to pyrazoles when heated with phosphorus tribromide in a sealed tube at higher temperatures they probably form intermediate products in the direct reduction of the pyrazolones. It is found that increased yields are obtained if yellow or red phosphorus is added to the tribromide.

The bispyrazolones are reduced to bispyrazoles if position 4 is occupied by oxygen, but fission of the molecule takes place with bis-4-alkylpyrazolones as also in the case of 4-benzylidenepyrazolones.

The 3-pyrazolones are reduced less easily than the pyrazolones, whilst with 1 : 5-diphenyl-3-pyrazolone the reaction leads to the formation of the bromopyrazole only.

Contrary to Stoermer's previous statement (*loc. cit.*), it is found now that the action of phosphorus tribromide on 1-phenyl-3 : 4 : 4-trimethylpyrazolone leads to the formation of 1-phenyl-3 : 4-dimethylpyrazole, b. p. 285—285·5° (275—278°: Steck, *Diss.*, *Jena*, 1896); the picrate, m. p. 122·5°; the platinichloride, m. p. 180—181° (decomp.); the methiodide, m. p. 162°, and the *aurichloride*, m. p. 166—167° were prepared.

1-*Phenyl*-3-*methyl*-4-*ethylpyrazole*, b. p. 294·5—295·5°, is obtained from the corresponding pyrazolone in a 55% yield; the *picrate*, yellow crystals, m. p. 129·5—130°; the *platinichloride*, small, yellowish-red crystals, m. p. 169°; the *aurichloride*, yellow needles, m. p. 141—142°.

1 : 4-*Diphenyl*-3-*methylpyrazole*, m. p. 41·5—42·5°, b. p. 220—224°/19 mm., is obtained from the 5-pyrazolone in a 45% yield.

1-Phenylpyrazole is formed in a 54% yield by the action of phosphorus tribromide and yellow phosphorus on 1-phenylpyrazolone at 215—225°.

The product, obtained on heating 1-phenyl-5-methyl-3-pyrazolone with phosphorus tribromide with or without the addition of red or yellow phosphorus, contains bromine which can be removed completely only on treatment with tin and hydrochloric acid. 1-Phenyl-5-methylpyrazole, obtained in this manner, b. p. 263·5°/762 mm. (corr.) (compare Claisen and Roosen, Abstr., 1894, i, 345; Bülow and Schlesinger, Abstr., 1900, i, 58; 1901, i, 98) and on oxidation, yields 1-phenylpyrazole-5-carboxylic acid. The platinichloride, m. p. 198—199°; the picrate, m. p. 97—98°, is formed together with a small amount of a *substance*, m. p. 192—193°; the *aurichloride* separates from alcoholic-hydrochloric acid in small crystals, m. p. 124—125°; the methiodide, m. p. 256—257° (287°: Bülow and Schlesinger, *loc. cit.*); the ethiodide, m. p. 208°. Claisen and Schlesinger's 1-phenyl-5-methylpyrazole was a mixture of this base with a small amount of 1-phenyl-3-methylpyrazole.

4 : 4′-*Bis*-1-*phenyl*-3-*methylpyrazole*, $C_{20}H_{18}N_4$, formed from 4 : 4′-bis-1-phenyl-3-methyl-5-pyrazolone, crystallises in white needles, m. p. 150°; the *picrate* forms scarlet needles, m. p. 159—160°; the *platinichloride*, small needles, decomposing when heated; the *aurichloride*, long needles, m. p. 207—208°. The *methiodide*, $C_{21}H_{21}N_4I$, crystallises in colourless leaflets, m. p. 236—237°; the *dimethiodide*, $C_{22}H_{24}N_4I_2$, forms small crystals, m. p. 182—183°, losing 1 mol. of methyl iodide, becomes brown on exposure to air, resolidifies when heated above its melting point, and then melts again at above 220° (decomp.).

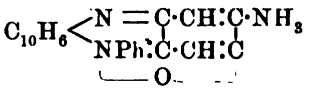
4 : 4-Bis-1 : 3-diphenylpyrazole, $C_{30}H_{22}N_4$, m. p. 231·5—232°, formed from the bispyrazolone in an almost theoretical yield, closely resembles Claisen and Roosen's 3 : 3′-bis-1 : 5-diphenylpyrazole (*loc. cit.*)

When heated with phosphorus tribromide and red phosphorus, 4 : 4′-bis-1-phenyl-3 : 4-dimethylpyrazolone and 4 : 4′-bis-1-phenyl-3-methyl-4-ethylpyrazolone yield 1-phenyl-3 : 4-dimethylpyrazole and 1-phenyl-3-methyl-4-ethylpyrazole respectively.

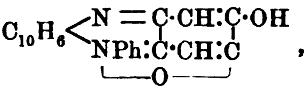
The action of phosphorus tribromide and red phosphorus on 1 : 1′-diphenyl-4 : 4′-benzylidene-3 : 3′-dimethyldipyrazolone leads to the formation of 1-phenyl-3-methylpyrazole and 1-*phenyl*-4-*benzyl*-3-*methylpyrazole*, $C_{17}H_{16}N_2$, which forms stout crystals, m. p. 62—63°, b. p. 260—270°, is readily soluble in organic solvents or concentrated acids, and gives the pyrazoline reaction. G. Y.

Preparation of 5 : 5-Dialkylbarbituric Acids. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 178934).—It is now found that dialkylbarbituric acids may be obtained by condensing dialkylmalonic esters and carbamide with disodium cyanamide. Ethyl diethylmalonate, carbamide, and disodium cyanamide intimately mixed and heated for three hours at 105—110° readily furnish 5 : 5-diethylbarbituric acid. G. T. M.

Action of Hydroxylamine on *iso*Rosindone. Friedrich Kehrmann and Hermann Prager (*Ber.*, 1907, **40**, 1234—1237. Compare Kehrmann and Gottrau, Abstr., 1905, i, 670; Fischer and Hepp, Abstr., 1900, i, 460; 1903, i, 654).—Contrary to the view of Fischer and Arntz (this vol., i, 94), the amino*iso*rosindone formed by the action of hydroxylamine on *iso*rosindone must have the constitution (I), as the corresponding hydroxy*iso*rosindone is identical with the product (II),



I.



II.

obtained by condensation of 4 : 5-dihydroxy-*o*-benzoquinone with phenylnaphthylenediamine. This observation is in opposition to Fischer and Arntz's statement that the action of alkyl iodides and potassium hydroxide on their hydroxy*iso*rosindone leads to the formation of ethers of naphthasafranol.

2-*Amino-5-hydroxy-*p-*benzoquinone*, $OH\cdot C_6H_2O_2\cdot NH_2$, prepared by heating aminohydroxybenzoquinoneimide with sodium hydroxide, is obtained as a brown, crystalline powder, decomposing at about 260°; it forms a brown solution in concentrated sulphuric acid, becoming rose-coloured on dilution, and is converted into dihydroxybenzoquinone when heated with sulphuric acid. It yields crystalline *condensation products* with alkylated *o*-diamines and *o*-aminophenols.

G. Y.

Preparation of a Hydriodide of 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone.

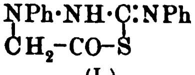
Giulio Nardelli and Vincenzo Paolini (D.R.-P. 180120) —4-*Dimethylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone hydriodide*, $C_{13}H_{17}ON_3,HI$, m. p. 205°, is produced by adding fuming hydriodic acid (sp. gr. 1·7) to a saturated aqueous solution of the pyrazolone derivative and evaporating the solution to dryness. The crystalline residue is very soluble in cold water, but dissolves only sparingly in hot alcohol, and is quite insoluble in ether, benzene, or ethyl acetate.

Owing to its great solubility in water, this salt is particularly useful in intravenous injections when, besides being a carrier of iodine, it also has antipyretic, antineuralgic, and antirheumatic properties.

G. T. M.

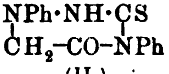
Inner Anhydrides of Thiosemicarbazide Acetic Acids.

Max Busch and Eduard Meussdörffer (*Ber.*, 1907, 40, 1021—1026). —*as*-Ethyl phenylhydrazinoacetate, $NH_2\cdot NPh\cdot CH_2\cdot CO_2Et$, combines with phenylthiocarbimide to form ethyl diphenylthiosemicarbazinoacetate, which, when saponified, yields, in addition to the corresponding acid, an anhydride for which the two formulæ



(I.)

and



(II.)

were suggested (Busch, Schneider, and Walter, Abstr., 1904, i, 97), formula I having been preferred.

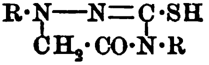
The behaviour of ethyl phenylthiosemicarbazinoacetate,

$$CO_2Et\cdot CH_2\cdot NPh\cdot NH\cdot CS\cdot NH_2,$$

and of ethyl phenylethylthiosemicarbazinoacetate,

$$CO_2Et\cdot CH_2\cdot NPh\cdot NH\cdot CS\cdot NHEt,$$

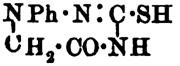
has now been studied. Each of these esters, when carefully saponified by alcoholic potassium hydroxide, yields, in addition to the corresponding acid, an inner anhydride. Each of these cyclic anhydrides exhibits a much greater stability towards alkali than does the diphenyl-compound referred to; they can be dissolved in cold alkalis and are not decomposed until they are warmed. The formation of disulphides shows that the compounds in question possess the properties of mercaptans. They accordingly react in the tautomeric form of formula II, namely, as of the annexed type.



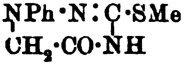
$$\begin{array}{l} R\cdot N—N{=}C\cdot SH \\ \;\;CH_2\cdot CO\cdot N\cdot R \end{array}$$

Ethyl phenylthiosemicarbazinoacetate, $C_{11}H_{15}O_2N_3S$, obtained from potassium thiocyanate and ethyl phenylhydrazinoacetate hydrochloride, forms white crystals, m. p. 115—116°.

Ketophenyltetrahydro-1 : 2 : 4-*triazinethiol*, obtained by saponifying the preceding ester and then acidifying the resulting potassium salt, separates from dilute alcohol in yellow leaflets, m. p. 172—173°. When its solution in alkali is acidified with acid, the original compound is precipitated. Its *methyl ether*, obtained by the action of methyl iodide on the potassium salt, separates from alcohol in glistening needles, m. p. 196—197° (decomp.).



$$\begin{array}{l} NPh\cdot N\colon C\cdot SH \\ CH_2\cdot CO\cdot NH \end{array}$$



$$\begin{array}{l} NPh\cdot N\colon C\cdot SMe \\ CH_2\cdot CO\cdot NH \end{array}$$

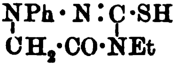
When oxidised by ferric chloride, ketophenyltetrahydro-1 : 2 : 4-triazinethiol forms the *disulphide*, $(C_9H_8ON_3)_2S_2$, which separates from ethyl acetate in glistening, yellow needles, m. p. 159°.

Phenylthiosemicarbazinoacetic acid, $CO_2H\cdot CH_2\cdot NPh\cdot NH\cdot CS\cdot NH_2$, obtained by gently warming the ester with dilute sodium hydroxide, separates from water in colourless crystals, m. p. 186° (decomp.).

Ethyl 1-*phenyl*-4-*ethylthiosemicarbazinoacetate*,

$$CO_2Et\cdot CH_2\cdot NPh\cdot NH\cdot CS\cdot NHEt,$$

obtained from ethyl thiocarbimide and *s*-ethyl phenylhydrazinoacetate, separates from a mixture of ether and light petroleum in transparent, monoclinic prisms, m. p. 84°. When saponified, it forms 1-*phenyl*-4-*ethyl*-5-*ketotetrahydro*-1 : 2 : 4-*triazinethiol*, which separates from a mixture of benzene and light petroleum in needles, m. p. 145°. It is a weak acid, which separates unchanged when its sodium salt in aqueous solution is acidified. Its *disulphide*, $(C_{11}H_{12}ON_3)_2S_2$, separates from alcohol in orange-red needles, m. p. 123°.



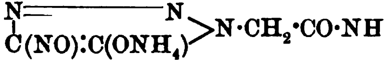
$$\begin{array}{l} NPh\cdot N\colon C\cdot SH \\ CH_2\cdot CO\cdot NEt \end{array}$$

Phenylethylthiosemicarbazinoacetic acid,

$$CO_2H\cdot CH_2\cdot NPh\cdot NH\cdot CS\cdot NHEt,$$

forms colourless crystals, m. p. 155°. A. McK.

Ammonium Salt of 5-Hydroxy-1 : 2 : 3-triazole-1-acetamide (1 : 2 : 3-Triazole-5-one-1-acetamide). THEODOR CURTIUS and ERNST WELDE (*Ber.*, 1907, 40, 1197—1200. Compare Abstr., 1906, i, 404, 940; this vol., i, 95).—The authors are unable to state at present whether the violet compound obtained by the action of sodium nitrite and acetic acid on ammonium 5-hydroxy-1 : 2 : 3-triazole-1-acetamide is a nitroso- or an *iso*nitroso-compound similar to Dimroth and Taub's ammonium 4-*iso*nitroso-1-phenyl-5-triazolone (*Ber.*, 1906, **39**, 1387); they regard it provisionally as ammonium 4-nitroso-5-hydroxy-1 : 2 : 3-triazole-1-acetamide,



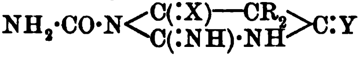
$$\genfrac{}{}{0pt}{}{N\!=\!=\!=\!=\!=\!=\!=\!=N}{|\qquad\qquad\quad\;\;}\!\!\!\genfrac{}{}{0pt}{}{}{C(NO){:}C(ONH_4)}\!>\!N\cdot CH_2\cdot CO\cdot NH_2$$

m. p. 138° (decomp.), not 120° (compare Abstr., 1906, i, 404). It forms anisotropic, violet-yellow, dichroic plates, does not give Liebermann's reaction, and by treatment with bromine water yields a colourless dibromo-compound which does not contain the NO or NH_4 groups and requires investigation.

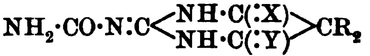
C. S.

Preparation of Pyrimidine Derivatives. Emanuel Merck (D.R.-P. 180119).—It has now been found that guanylcarbamide condenses readily with dialkylmalononitriles, dialkylmalonyl chlorides, or ethyl cyanodialkylacetates, this reaction taking place either with or without the addition of alkalis.

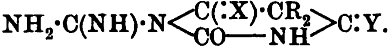
Guanylcarbamide hydrochloride and ethyl cyanodiethylacetate, when condensed in alcoholic sodium ethoxide, yield a product which decomposes above 300° and dissolves in acids or alkalis, although very sparingly soluble in water, ether, or alcohol. On acid hydrolysis, it furnishes a good yield of diethylbarbituric acid. Guanylcarbimide hydrochloride and diethylmalononitrile yield a similar condensation product, which decomposes at 230—232° and gives diethylbarbituric acid on hydrolysis. With free guanylcarbamide and diethylmalonyl chloride a pyrimidine derivative is obtained, which decomposes above 350° and is hydrolysed by mineral acids. These condensation products are not homogeneous substances, but contain mixtures of compounds having the following formulæ:



$$NH_2\cdot CO\cdot N\!<\!\genfrac{}{}{0pt}{}{C({:}X)\text{—}CR_2}{C({:}NH)\cdot NH}\!>\!C{:}Y$$



$$NH_2\cdot CO\cdot N{:}C\!<\!\genfrac{}{}{0pt}{}{NH\cdot C({:}X)}{NH\cdot C({:}Y)}\!>\!CR_2$$



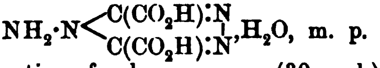
$$NH_2\cdot C(NH)\cdot N\!<\!\genfrac{}{}{0pt}{}{C({:}X)\cdot CR_2}{CO\text{——}NH}\!>\!C{:}Y.$$

These possibilities arise from the tautomeric nature of guanylcarbamide, $NH_2\cdot CO\cdot NH\cdot C({:}NH)\cdot NH_2$ and $NH_2\cdot CO\cdot N{:}C(NH_2)_2$.

All the condensation products obtained, however, by the foregoing condensation with this base readily yield 5 : 5-dialkylbarbituric acids.

G. T. M.

1-Amino-1 : 3 : 4-triazole-2 : 5-dicarboxylic Acid. Theodor Curtius, August Darapsky, and Ernst Müller (*Ber.*, 1907, **40**, 1194—1197. Compare this vol., i, 359).—The potassium salt of a dibasic acid isomeric with bisdiazoacetic acid, obtained by Hantzsch and Silberrad (Abstr., 1900, i, 261) by the prolonged action of concentrated potassium hydroxide on ethyl diazoacetate, is the normal salt of 1-amino-1 : 3 : 4-triazole-2 : 5-dicarboxylic acid. The free *acid*,

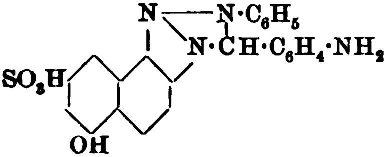


$$NH_2\cdot N\!<\!\genfrac{}{}{0pt}{}{C(CO_2H){:}N}{C(CO_2H){:}N}\!\!\Big|\;,H_2O$$

m. p. 77° (decomp.), is obtained by the action of a large excess (30 mol.) of 30% sulphuric acid at 0°. It crystallises in colourless, glistening needles and decomposes with extraordinary ease; by treatment with hydrochloric or sulphuric acid, warm water, or alcohol it loses carbon dioxide, and at its melting point decomposes into water, carbon dioxide, and 1-amino-1 : 3 : 4-triazole. By the action of potassium hydroxide on an aqueous solution of the acid the normal potassium salt is regenerated. C. S.

Preparation of Aminoaryl Derivatives of 5-Hydroxy-1 : 2-Naphthatriazine-7-sulphonic Acid. LEOPOLD CASSELLA & CO. (D. R.-P. 180031).—6-Amino-α-naphthol-3-sulphonic acid gives rise to a series of hydroxynaphthatriazines containing amino-groups attached to the aromatic nuclei in the triazine ring. On account of this constitution, these complex triazines couple with diazo-compounds in alkaline solutions to furnish azo-derivatives which are diazotisable.

The *triazine* is produced by coupling diazobenzene chloride with 6-amino-α-naphthol-3-sulphonic acid in acid solution and then condensing the intermediate azo-compound with *m*-aminobenzaldehyde. The free triazine-sulphonic acid is sparingly soluble in water, but its sodium salt dissolves readily in this medium.



The patent describes the preparation of other complex triazines of the foregoing type containing one or more amino-groups attached to the benzene nuclei. G. T. M.

Notes on Bülow's Papers: "So-called Dihydrotetrazines" and "Decomposition Products of Acylhydrazones of Esters of 1 : 3-Ketocarboxylic Acids." THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, **40**, 1470—1477. Compare Abstr., 1906, i, 939; this vol., i, 21, 262, 359; also Bülow, Abstr., 1906, i, 905; this vol., i, 99).—Dihydrotetrazine is probably 1-aminotriazole, but conclusive evidence for this view has not been brought forward; Pinner (Abstr., 1898, i, 94), Stollé (*J. pr. Chem.*, 1906, [ii], **73**, 277), and Busche (Abstr., 1901, i, 488, 616) have shown that compounds previously supposed to contain a six-membered ring can be more conveniently represented as amino-derivatives of a five-membered ring system.

It is pointed out that the genetic relationship between 1-aminotriazole and the so-called dihydrotetrazinedicarboxylic acid does not prove the constitution of the latter compound, since the six-membered ring system of bisdiazoacetic acid at its melting point or even at 100° can be converted into 1-aminotriazole. It is, however, highly probable that the so-called dihydrotetrazinedicarboxylic acid is 1-aminotriazoledicarboxylic acid, as it yields 1-aminotriazole at the ordinary temperature.

Several of the compounds prepared by Bülow have been previously described and investigated by Wolff (Abstr., 1904, i, 722). J. J. S.

Hydrolysis of 1 : 2 : 4 : 5-Tetrazine-3 : 6-dicarboxylic Acid. THEODOR CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1907, **40**, 1176—1193).—The hydrolysis of tetrazinedicarboxylic acid by water is a much more complicated process than that of its amide (compare Abstr., 1906, i, 939). According to Hantzsch and Lehmann (Abstr., 1901, i, 132), the hydrolysis of the acid (which they call bisazoxyacetic acid) yields hydraziacetic acid: $C_4H_4O_6N_4 + H_2O = C_2H_4O_2N_2 + N_2 + 2CO_2 + H_2O$; in the presence of acid, the hydraziacetic acid decomposes into hydrazine and oxalic acid.

The authors question this interpretation of the hydrolysis. In the first place the salts of hydraziacetic acid are hydrolysed readily, yielding hydrazine and glyoxylic acid (Curtius and Jay, Abstr., 1894, i, 324). Also only one-third of the nitrogen in tetrazinedicarboxylic acid is liberated in the elementary state during hydrolysis, together with traces of carbon dioxide. They find that Hantzsch and Lehmann's hydraziacetic acid is the *hydrogen hydrazine* salt of the oxalylhydrazone of glyoxylic acid, $CO_2H\cdot CH{:}N\cdot NH\cdot CO\cdot CO_2H,N_2H_4$, m. p. 243° (decomp.). The substance is obtained in better yield by rapidly boiling tetrazinedicarboxylic acid with water, and is synthesised by treating a warm aqueous solution of hydrazino-oxalic acid with the calculated quantity of a 3% solution of glyoxylic acid and, after cooling, with hydrazine hydrate. The methyl ester, $C_5H_6O_5N_2$, obtained from the silver salt, has m. p. 117° (Hantzsch and Lehmann, 102°), and is not converted by mercuric oxide into ethyl diazoacetate.

Benzylidenehydrazino-oxalic acid, $CHPh{:}N\cdot NH\cdot CO\cdot CO_2H$, m. p. 179—180°, obtained by decomposing tetrazinedicarboxylic acid with water at 30° and adding benzaldehyde, forms long, white needles, and is decomposed by dilute hydrochloric acid, yielding benzaldehyde, hydrazine, and oxalic acid.

Hydrazino-oxalic acid hydrochloride, $CO_2H\cdot CO\cdot NH\cdot NH_2,HCl$, prepared by triturating the preceding compound with concentrated hydrochloric acid, forms a white, crystalline mass, sinters at 121°, and has m. p. 128—129° (decomp.). Its aqueous solution and benzaldehyde form the benzylidene compound, whilst from the solution in boiling water separate colourless crystals of *hydrazino-oxalic acid*, $NH_2\cdot NH\cdot CO\cdot CO_2H$, m. p. >300°, the *silver* salt of which, $C_2H_3O_3N_2Ag$, is stable to light.

The hydrolysis of tetrazine itself by water is not a simple process. The anticipated products would be one molecule each of formaldehyde, formic acid, hydrazine, and nitrogen, with the intermediate production of formaldehydeformylhydrazone; the products actually obtained do not include formaldehyde, and contain more hydrazine and less nitrogen than the above-mentioned quantities. The investigation of the reaction is still in progress.

The authors cannot confirm Hantzsch and Lehmann's statement (*loc. cit.*) that their so-called hydraziacetic acid results by the reduction of bisdiazoacetic acid or of tetrazinedicarboxylic acid by sodium amalgam at 0°.

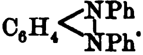
When bisdiazoacetic acid is crystallised from water, yellow crystals of the hydrated acid, m. p. 149—155°, are deposited; from the filtrate, after long keeping, slender, yellow needles are obtained consisting of *hydrogen hydrazine bisdiazoacetate*, m. p. 188—189° (decomp.); the same salt is formed from bisdiazoacetic acid by prolonged boiling with water or by treatment with the requisite quantity of hydrazine. The substance yields tetrazinedicarboxylic acid with nitrous acid, benzylideneazine with benzaldehyde, and bisdiazoacetic acid when its alkaline solution is acidified.

Hantzsch and Silberrad seem to have mistaken this salt for anhydrous bisdiazoacetic acid (Abstr., 1900, i, 261). The latter is obtained by treating the hydrated acid with absolute alcohol, filtering, and evaporating the filtrate in a vacuum over sulphuric acid; it forms strongly polarising, yellow, prismatic crystals, and has the same melting point as the hydrated acid. Both acids are converted into 1-amino-1 : 3 : 4-triazole at 100°, whereas the hydrogen hydrazine salt is stable at this temperature. C. S.

Action of Potassium Ferrocyanide on Diazo-salts. A. Ehrenpreis (*Bull. Acad. Sci., Cracow*, 1906, 265—270).—Griess (this Journ., 1876, i, 932) found that diazobenzene chloride is decomposed by potassium ferrocyanide in aqueous solution with formation of nitrogen, azobenzene, and a red oil. The author has studied this reaction and extended it to other diazonium salts.

Reduction of the red oil from diazobenzene chloride, with zinc dust and a small amount of ammonia in alcoholic solution, leads to the formation of *triphenylhydrazine*, $NPh_2\cdot NHPh$, which separates in hard, glistening crystals, m. p. 136—138°, yields an *acetyl* derivative,

$$C_{18}H_{15}N_2Ac,$$

needles, m. p. 152·5°, and, when treated with stannous chloride in concentrated hydrochloric acid, undergoes the semidine transformation, forming *aminotriphenylamine*, $NH_2\cdot C_6H_4\cdot NPh_2$, m. p. 136°. This gives reactions for a primary base and is readily acetylated. When oxidised with mercuric oxide in benzene solution, triphenylhydrazine forms a red oil, b. p. 270°, which is identical probably with the product of the action of potassium ferrocyanide on diazobenzene chloride; it may have the constitution  $C_6H_4{<}\begin{array}{l}NPh\\ \vert\\ NPh\end{array}$.

Contrary to the statement of Bandrowski and Prokopeczko (Abstr., 1904, i, 635), the derivatives of benzenehydrazodiphenyl, m. p. 217° and 178°, are isomeric mono- and not di-acetyl compounds.

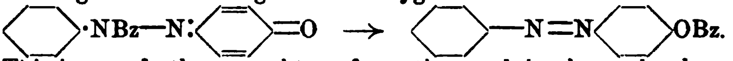
When treated with potassium ferrocyanide in aqueous solution, *o*-diazotoluene chloride yields o-*tolueneazo*-2 : 2′-*dimethyldiphenyl*,

$$C_6H_4Me\cdot C_6H_3Me\cdot N_2\cdot C_6H_4Me,$$

red crystals, m. p. 104°, and a red *oil*. Under the same conditions, *p*-diazotoluene chloride yields p-*tolueneazo*-4 : 4′-*dimethyldiphenyl*, m. p. 118°, and a red *oil*. The *product*, obtained on reduction of this, is very readily oxidised.

The action of potassium ferrocyanide on *m*-diazotoluene chloride leads to the formation of a brown, viscid *oil*, which can be distilled, and forms a *hydrochloride*, $C_{15}H_{18}NCl$, crystallising in silver-white plates. G. Y.

Quinonoid Compounds. XII. Tarnsformation of Benzoquinonephenylhydrazones into Oxyazo-compounds. Richard Willstätter and Hans Veraguth (*Ber.*, 1907, **40**, 1432—1437).—When a cold dry ethereal solution of benzoquinonebenzoylphenylhydrazone is shaken with powdered potassium hydroxide for twenty-four hours, it is converted into benzoxyazobenzene, the acyl group wandering from the nitrogen to the oxygen atom :



This is a perfectly general transformation and is shown by benzoquinonephenylcarbethoxyhydrazone, $O:C_6H_4:N\cdot NPh\cdot CO_2Et$, and benzoquinoneacetylphenylhydrazone, the change in these cases taking place best in the boiling ethereal solution.

These results are in opposition to the views of Farmer and Hantzsch (Abstr., 1900, i, 122), as there is no reason to suppose free oxyazobenzene as unstable when the *N*-acyl quinonoid derivative is the less stable isomeride. McPherson's conclusions (Abstr., 1900, i, 133) as to the constitution of oxyazobenzene, based on the hydrolysis of benzoquinonephenylhydrazones, are also invalidated in the light of these results.

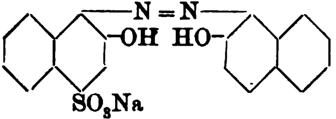
Benzoquinonephenylcarbethoxyhydrazone, prepared by the condensation of ethyl formate phenylhydrazide (m. p. 24—25°) and benzoquinone, crystallises in yellow prisms, m. p. 96—97°.

W. R.

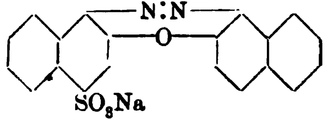
Preparation of 2′-Hydroxynaphthalene-1-azo-β-naphthol-4′-sulphonic Acid. ANILINFARBEN- & EXTRACT-FABRIKEN VORMALS J. R. GEIGY (D.R.-P.177925).

—*2′-Hydroxynaphthalene-1-azo-β-naphthol-4′-sulphonic acid*, prepared by combining 1-diazo-β-naphthol-4-sulphonic acid with alkaline-β-naphthol, separates in the form of its *disodium* salt which is not suitable for dyeing purposes. The *monosodium* salt (I), obtained by cautiously neutralising the disodium salt with a mineral acid or by acidifying its solution with acetic acid, is unstable and passes readily into the sparingly soluble anhydro-compound (II)

(I)



(II)



which separates in copper-coloured crystals.

It is now found that the free sulphonic acid can be precipitated in the form of a hydrogen chloride additive compound by adding excess of hydrochloric acid to the aqueous solution of the monosodium salt. On gently heating, this additive product loses hydrogen chloride and furnishes the free sulphonic acid, a greenish-black powder with a bronze reflex which is soluble even in cold water. Its aqueous solution is stable at 100°, but the addition of sodium chloride or sulphate at 60—70° determines the formation of the sparingly soluble sodium salt of the anhydro-compound. G. T. M.

Water in Proteins. FRANCIS G. BENEDICT and CHARLOTTE R. MANNING (*Amer. J. Physiol.*, 1907, 18, 213—221).

—The hygroscopic nature of proteins renders the usual process of drying by heating in an air-bath at 110° useless in exact work. This error may be as high as 1%. The removal of final traces of moisture can be effected by subsequent desiccation in a high vacuum for two weeks. The experiments recorded were made with gelatin, collagen, elastin, edestin, legumin, and conglutin. In many cases after desiccation at room temperature in a high vacuum until constant weight was reached (about two weeks), a subsequent stay in an air-bath at 100° for a few hours caused them to take up water again in small amount. This is again removable by a high vacuum for two weeks. No oxidation or volatilisation could be detected when the heating lasted for five hours. W. D. H.

Hydrolysis of Phaseolin. THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, 18, 295—308).—Phaseolin, formerly called legumin, is a globulin, and forms nearly all the protein substance of the white kidney bean. The following substances were obtained on hydrolysis; the figures are percentages calculated on a water-free and ash-free basis: glycine, 0·55; alanine, 1·8; valine, 1·04; leucine, 9·65; proline, 2·77; phenylalanine, 3·25; aspartic acid, 5·24; glutamic acid, 14·54; serine, 0·38; tyrosine, 2·18; arginine, 4·89; histidine, 1·97; lysine, 3·92; ammonia, 2·06: total 54·27. Oxyproline and tryptophan were present, but not estimated. The figures coincide very well with those published by Abderhalden and Babkin on the legumin of the white bean. W. D. H.

Reduction of Derivatives of the Colouring Matter of Blood by Means of Zinc and Hydrochloric Acid. J. MERUNOWICZ and JEAN ZALESKI (*Bull. Acad. Sci., Cracow*, 1906, 729—733).—Hoppe-Seyler (Abstr., 1889, 787) and Nencki and Sieber (Abstr., 1888, 971) showed that on reduction in acid solution, hæmatoporphyrin yields a yellow solution which gives reactions for urobilin, but differs from this in undergoing change to reddish- or violet-brown on exposure to air. The authors have observed that this change of colour takes place most easily when hæmato- or meso-porphyrin is reduced by means of zinc dust; the reduced solution is colourless and optically inactive; the change of colour through yellow to reddish-brown takes place equally in acid or alkaline solution. As the absorption spectrum of the yellow solution exhibits urobilin bands, whilst the reddish-brown solution shows in addition bands of the spectrum of acid, or alkaline, porphyrin, the authors separated the porphyrin formed in this manner by oxidation of the leuco-compound, and find it to be identical with the hæmato- or meso-porphyrin reduced. Hæmin undergoes similar changes when reduced with zinc dust in alcoholic-acetic acid solution, yielding on exposure to air solutions giving the spectra of urobilin and hæmatoporphyrin, whilst if the hæmin is reduced in acetic and hydriodic acids meso-porphyrin is formed by the oxidation. With iodine or bromine, the colourless solution of the leuco-compound yields mixtures of amorphous *substances* which are soluble in alcohol, but insoluble in water.

From the amount of oxygen absorbed by reduced meso-porphyrin it is concluded that the leuco-compound contains 4 atoms of hydrogen more or 2 atoms of oxgen less than the dye. G. Y.

Reaction Velocity Between Opsonin and Red Blood Corpuscles. J. O. Wakelin Barratt (*Zeitsch. physikal. Chem.*, 1907, **58**, 467—474).—The velocity with which red blood corpuscles combine with opsonin (compare *Proc. Roy. Soc.*, 1907, B, **79**) has been determined, and, although the reaction is heterogeneous, it appears to be bimolecular. The various possibilities, for example, the colloidal or crystalloid nature of the active constituent of the corpuscles, the colloid or crystalloid nature of opsonin, the reaction depending on diffusion, adsorption, or chemical action, are discussed. J. J. S.

Catalytic Decomposition of Hydrogen Peroxide by the Catalase of the Blood. C. A. Lovatt Evans (*Biochem. J.*, 1907, **2**, 133—155).—For each concentration of enzyme there is an optimum concentration of hydrogen peroxide. The optima do not vary directly as the enzyme concentrations, but more nearly as their square roots. The numerous departures from the rule, however, necessitate the introduction of more complicated hypotheses. W. D. H.

An Enzyme in Cortinellus Edodes which Splits Nucleic Acid. T. Kikkōji (*Zeitsch. physiol. Chem.*, 1907, **51**, 201—206).—Nuclease has already been described as occurring in yeast and other fungi; the enzyme now described in a Japanese fungus is probably the same ferment. It splits nucleic acid with the formation of purine bases and phosphoric acid; it is destroyed by heat; it acts best in a neutral or faintly acid medium; it is inhibited by 0·5% acetic acid and by 0·5% sodium carbonate. In neutral solution it is salted out by ammonium sulphate. W. D. H.

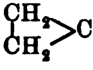
Action of Light on Invertin in the Absence and Presence of Cane Sugar and other Substances. A. Jodlbauer (*Biochem. Zeitsch.*, 1907, **3**, 488—502)—The presence of sucrose inhibits the destructive influence of light on invertin. Solutions of sodium chloride, sodium sulphate, carbamide, and glycerol, equimolecular with a 20% sucrose solution, produce no such effect. Glycine also has no action, but mannitol has a slight inhibiting effect. Dextrose, lævulose, *d*-mannose, *d*-galactose, lactose, and maltose act similarly to sucrose; starch and dextrin have no effect. All the substances mentioned however, increase the resistance of the enzyme towards destruction by heat. W. D. H.

Influence of Oxygen on the Destruction of Ferments (Invertin) by Heat. A. Jodlbauer (*Biochem. Zeitsch.*, 1907, **3**, 483—487).—The effect of various parts of the spectrum on invertin rendered necessary the investigations of the question stated in the title. The destruction was found to be equal whether oxygen or hydrogen was present. The destruction by the visible rays of the spectrum occurs only in the presence of oxygen. Photolability and thermolability are thus different phenomena. W. D. H.

Organic Chemistry.

Equilibrium of Methane. M. MAYER and V. ALTMAYER (*Ber.*, 1907, **40**, 2134—2144).—The reaction $C + 2H_2 \rightleftarrows CH_4$ in the presence of nickel or cobalt has been studied from both sides of the equation at temperatures between 470° and 620°. The authors develop the equation $CT = -18507 + 5\cdot9934T\log T + 0\cdot002936T^2 + RT\log p/p_1^2$, where p and p_1 represent the partial pressure of methane and of hydrogen at the temperature T. The average value of the constant C is 21·6 with nickel as catalyst and 21·1 with cobalt in those experiments in which the initial gas is methane; $C = 20\cdot8$ with each catalyst when the initial gas is hydrogen.

Putting $C = 21\cdot1$ in the equation, the authors calculate that under one atmosphere the % of CH_4 at 250° is 98·79, and at 850°, 1·59. Hence doubts are expressed as to Bone and Jerdan having really effected the synthesis of methane at 1200° (Trans, 1897, **71**, 41), the suggestion made being that the carbon employed contained impurities which yielded methane.
C. S.

Catalytic Reactions at High Temperatures and Pressures. XIII. Catalytic Isomerisation of Butylene. WLADIMIR IPATIEFF and W. SDZITOWECKY (*Ber.*, 1907, **40**, 1827—1830. Compare Abstr., 1903, i, 593, 594; this vol., i, 6).—Whilst the decomposition of *iso*butyl alcohol in contact with alumina leads to the formation of *iso*butylene only, which is formed also by the decomposition of trimethylcarbinol, a mixture of the three butylenes is obtained when *iso*butyl alcohol is passed through a copper tube containing zinc chloride. This does not result from isomerisation of *iso*butylene first formed, since it was found that the butylenes do not undergo isomerisation when passed over zinc chloride at various temperatures. It is now found that *sec.*-butyl alcohol when passed through a copper tube containing alumina at 450° yields β-butylene and only traces of *iso*butylene, but if passed over zinc chloride at the same temperature forms β-butylene together with considerable quantities of *iso*butylene, methyl ethyl ketone, and a liquid, unsaturated hydrocarbon, which is probably the product of the decomposition of an ether formed in the first stage of the reaction (compare Abstr., 1904, ii, 645). It is considered that under the influence of the strong dehydrating action of the zinc chloride a portion of the *sec.*-butyl alcohol loses water in such manner as to form the *cyclo*propane derivative,  $\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>CHMe$, which undergoes isomerisation into *iso*butylene.

sec.-Butyl alcohol, free from *tert.*-butyl alcohol, is prepared by the action of hydrogen on methyl ethyl ketone in presence of nickel oxide. Contrary to Scheschukoff's statement (Abstr., 1886, 680), *sec.*-butyl iodide dissolves in hot water, being hydrolysed to *sec.*-butyl alcohol.
G. Y.

Physical Properties of Liquid and Solid Acetylene. Douglas McIntosh (*J. Physical Chem.*, 1907, **11**, 306—317).—The author has determined the most important physical constants of acetylene. The sublimation temperature of solid acetylene is − 83·6°, m. p. − 81·5° (under a pressure of 895 mm.). From Clausius' equation the heat of vaporisation of the liquid is calculated to be $21{\cdot}3 \times 10^{10}$ ergs., that of the solid, $23{\cdot}0 \times 10^{10}$ ergs. Direct measurement of the former quantity gave $21{\cdot}0 \times 10^{10}$ ergs. The specific heat of liquid acetylene between − 78·5° and − 73° is equivalent to $4{\cdot}4 \times 10^{7}$ ergs. The liquid has D^{-80} 0·613; solid, D^{-80} 0·72. Critical temperature, 36·5°; critical pressure, 61·6 atmospheres; critical volume, 83 c.c. The constants *a* and *b* of van der Waals' equation are 0·0880 and 0·00230 respectively.

From the high value of the molecular volume of acetylene (42) the author concludes that acetylene contains a bivalent carbon atom, and has the constitution of acetylidene, $C{:}CH_2$. The atomic volume of bivalent carbon in acetylene is therefore about 20, which agrees with the value obtained from the molecular volume of liquid carbon monoxide.

Acetylene forms crystalline compounds with ethyl ether, ethyl alcohol, acetone, and with the halogen hydrides (?) at low temperatures. The great solubility of the hydrocarbon in many organic liquids is probably connected with this property. Liquid acetylene is a non-conducting and non-ionising solvent.

Incidentally, an electrically controlled Dewar tube thermostat is described by means of which temperatures from − 70° to − 95° can be readily maintained constant to between 0·3° and 0·4°. H. M. D.

Determination of Melting Points at Low Temperatures. II. Leo F. Guttmann (*J. Amer. Chem. Soc.*, 1907, **29**, 345—348).—The following m. p's. have been determined by the method described previously (Trans., 1905, **87**, 1037). Methyl alcohol, − 97·8°; ethyl alcohol, − 117·3°; methyl acetate, − 98·7°; ethyl acetate, − 82·8°; propyl acetate, − 92·5°; pentane, − 147·5°; hexane, − 93·5°; octane, − 98·2°; ethyl ether, − 117·6°; ethyl bromide, − 117·8°; methyl iodide, − 64·4°; ethyl iodide, − 108·5°; *n*-propyl iodide, − 98·8°; *iso*propyl iodide, − 89° to − 91·8°; *iso*butyl iodide, − 90·7°; ethyl formate, − 78·9°; ethyl propionate, − 72·6°; ethyl butyrate, − 93·3°; acetaldehyde, − 124·6°; acetone, − 94·6°; and methyl ethyl ketone, − 85·9°. The results of these determinations show the value of the m. p. as a criterion of purity. Of the alcohols, methyl and ethyl alcohols give a m. p., but with propyl, *iso*butyl, and *iso*amyl alcohols no definite m. p. is obtainable, owing probably to their being composed of mixtures of various isomerides. The esters and alkyl iodides are more readily obtainable in a pure state. It is noteworthy that ethyl alcohol, ethyl ether, and ethyl bromide have almost the same m. p. E. G.

Direct Hydrogenation of Allyl Compounds. Paul Sabatier (*Compt rend*, 1907, **144**, 879—881. Compare this vol., i, 488, 490).—Of the reactions of direct hydrogenation in presence of reduced nickel the one most easily effected is the addition of hydrogen to an ethylenic linking, and in an ethylenic compound, capable of hydrogenation in a second manner, it is possible to effect the reduction of the ethylenic bond alone (compare Haller and Martine, Abstr., 1905, i, 533; Darzens, Abstr., 1905, i, 172; this vol., i, 277; Sabatier and Senderens, Abstr., 1905, i, 333). When allyl alcohol vapour mixed with hydrogen is passed over reduced nickel at 130—170°, it is completely reduced to propyl alcohol containing a small quantity of propaldehyde. The same reaction is effected, much less rapidly, by means of reduced copper at above 180°. Allyl oxide is similarly reduced by nickel at 135—140° to propyl oxide, but the allyl halides are decomposed with separation of the haloid acid. E. H.

Addition of Hydrogen Chloride to *iso*Butylene Oxide. K. KRASSUSKY (*J. pr. Chem.*, 1907, [ii], 75, 238—247. Compare Abstr., 1901, i, 246; 1902, i, 8).—A criticism of the work of Henry (Abstr., 1906, i, 228; this vol., i, 7) and of Michael and Leighton (Abstr., 1906, i, 551, 781). The results obtained on reinvestigation of the action of hypochlorous acid and of hydrogen chloride on *iso*butylene oxide are in agreement with the author's previous statements. The product of the action of hydrogen chloride on *iso*butylene oxide consists of chlorotrimethylcarbinol, traces of condensation products of *iso*butaldehyde, and an *oil*, b. p. 132—136°, which is insoluble in water and is not a chlorohydrin, since it does not yield an oxide when distilled over potassium hydroxide. An insoluble, white, amorphous *substance*, m. p. 142—144°, is obtained if the turbid liquid, formed by saturating *iso*butylene oxide, cooled by ice-water, with hydrogen chloride, is treated with ether. The chloro-compound, C_4H_7Cl, obtained by distilling the chlorohydrin over phosphoric oxide, forms a *dibromide*, $C_4H_7ClBr_2$. G. Y.

***tert.*-Pinacolyl Alcohol.** MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 455—461. Compare Abstr., 1906, i, 476, 551, 784, 921, and Henry, Abstr., 1906, i, 329).—*tert.*-Pinacolyl alcohol (dimethyl*iso*propylcarbinol), $CHMe_2{\cdot}CMe_2{\cdot}OH$, b. p. 118—118·6°, m. p. −12°, obtained by the action of magnesium *iso*propyl bromide on acetone, on treatment with acetic anhydride furnishes an *acetate*, b. p. 139—143°, which, when warmed with powdered potassium hydroxide, regenerates the alcohol unchanged. The latter is not reduced by metallic sodium, and, when treated with bromine in presence of ice or cold water, furnishes a *substance*, b. p. 115—119°. If cold water or ice is not employed the principal product is a crystalline bromide, m. p. 132—133°. The alcohol yields a crystalline *urethane*, m. p. 65—66°.

sec.-Pinacolyl alcohol (methyl*tert.*-butylcarbinol), $CMe_3{\cdot}CHMe{\cdot}OH$, on treatment with acetyl chloride, furnishes an *acetate*, b. p. 135—143°, and this, when warmed with powdered potassium hydroxide, regenerates the *sec.*-alcohol unchanged, b. p. 117—121°, which, on treatment with bromine in presence of ice, furnishes pinacolin, b. p. 107—110°, but if ice is not employed the principal product is a crystalline *bromide*, m. p. 132—133°, closely resembling that obtained from the *tert.*-alcohol under similar conditions. The *sec.*-alcohol furnishes a crystalline *urethane*, m. p. 76—77°. T. A. H.

Preparation of Alkyloxyglycols. AUGUSTE BÉHAL and MARCEL SOMMELET (D.R.-P. 180202. Compare this vol., i, 275).—The process now described is a modification of the method formerly employed in the production of the alkyloxyglycols. It consists in subjecting halogenated methyl alkyl ethers to the action of ketones, nitriles, or acid amides in the presence of metals or organo-metallic compounds.

β-Hydroxy-a-ethoxy-β-methyldecane, $C_8H_{17}\cdot CMe(OH)\cdot CH_2\cdot OEt$, b. p. 140—150°/20 mm., is produced by slowly adding chloromethyl ethyl ether to a mixture of pelargononitrile and magnesium in dry ether.

β-Hydroxy-a-ethoxy-β-methylundecane, $C_9H_{19}\cdot CMe(OH)\cdot CH_2\cdot OEt$, b. p. 153—155°/17 mm., and *β-Hydroxy-a-ethoxy-β-methyldodecane*, b. p. 160—162°/15 mm., are obtained respectively from methyl nonyl ketone and methyl decyl ketone. G. T. M.

Determination of the Limits of Inflammability of Explosive Mixtures of Ethyl Ether Vapour and Air. JEAN MEUNIER (*Compt. rend.*, 1907, **144**, 796—798).—The author has applied a modification of the method previously used (*Compt. rend.*, 1900, **131**, 727) with mixtures of hydrocarbon vapours and air to mixtures of ethyl ether vapour and air. Air containing 0·045 gram of ethyl ether vapour per litre does not inflame; when the proportion of ether amounts to 0·09 gram per litre there is a clear ignition giving a blue flame which is rapidly propagated in the explosion vessel; with 0·135 gram of ether per litre the combustion is explosive, accompanied by a blue flame, which is very rapidly propagated; with 0·180 gram of ether per litre the combustion is explosive, but the flame is green, indicating an excess of ether vapour; air containing 0·225 gram of ether per litre is not inflammable, and extinguishes a lighted taper. One litre of air at 15° is theoretically necessary for the combustion of 0·098 gram of ether. The author concludes that the limits of inflammability of ether in air are approximately 0·075 and 0·2 gram of vapour per litre. On the results obtained is based a method for the determination of the proportion of ether vapour in mixtures with air. E. H.

Limit of Inflammability of Mixtures of Ether Vapour and Air. OCTAVE BOUDOUARD and HENRI LE CHATELIER (*Compt. rend.*, 1907, **144**, 910—911. Compare Meunier, preceding abstract).—The authors draw attention to the fact that they have determined previously (Abstr., 1898, ii, 574) the inferior limit of inflammability of ether vapour in air to be 0·06 gram per litre. E. H.

Formation of Double Salts in Solvents other than Water. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 403—408).—The author describes double salts having the compositions: $CuCl_2,LiCl,HCO_2H$; $CuCl_2,LiCl,CH_3\cdot CN$; $CdI_2,2NaI,9COMe_2$; $CoI_2,2NaI,9COMe_2$; $CdI_2,2NaI,6Ac_2O$; $CoI_2,NaI,6Ac_2O$, and $CoI_2,NaI,3Ac_2O$. The formulæ of the two salts crystallising with acetone are indicated by that of the salt $CoI_2,9H_2O$ (Bolschakoff, Abstr., 1899, ii, 427), as it is often found, for example, with the carnallites, that the number of mols. of water of crystallisation in the double salt is the same as in the crystalline hydrate of the salt of the bivalent metal. That acetone mols. can replace an equal number of water mols. is rendered probable by our knowledge of oxonium salts (Schmidt, *Basische Eigenschaften des Sauerstoffs und Kohlenstoffs*, 1904, 23). No hydrated double salt is known corresponding with the salt $CoI_2,NaI,3Ac_2O$, although the compound $CdI_2,HI,3H_2O$ (Dobroserdoff, Abstr., 1900, ii, 654) has been obtained. The difference in colour between the two salts, $CoI_2,NaI,3Ac_2O$ and $CoI_2,2NaI,6Ac_2O$, which are green and reddish-brown respectively, recalls the colour phenomena observed in aqueous solutions of cobalt iodide, bromide and chloride when the concentration and temperature are varied. T. H. P.

Behaviour of Sodium and Sodium Alkyloxides towards Various Esters of Acetic Acid. LOUIS ALLEN HIGLEY (*Amer. Chem. J.*, 1907, **37**, 293—324).—Nef has shown (Abstr., 1902, i, 6) that the alkylation of anilines by sodium alkyloxides is due to the alkylidene dissociation of the latter. Thus, in the alkylation of acetylethylaniline the alkylidene residue unites directly with the anilide, $R\cdot CH< + H\cdot CH_2\cdot CO\cdot NPhEt \longrightarrow R\cdot CH_2\cdot CH_2\cdot CO\cdot NPhEt$. It is evident, however, from the work of Geuther and Claisen with ethyl acetate and sodium ethoxide that these reactions might be due to an intermediate formation of ethyl acetoacetate. This compound would unite immediately with the alkylidene present to form mono- and dialkylacetoacetic esters, which in the presence of the sodium hydroxide would give rise to mono- and di-alkylacetic acids. It has now been proved that this intermediate formation of ethyl acetoacetate does actually occur when acetethylanilide is heated with sodium alkyloxides at 100°. There are cases, however, where the alkylation must take place directly. Thus in the alkylation of the formyl group and in the replacement of the tertiary hydrogen atom in the *iso*butyl group, the formation of an acetoacetic acid derivative is impossible.

It has been shown by Nef (Abstr., 1898, i, 112) that the reaction between ethyl acetate and sodium ethoxide proceeds as follows and is reversible: $CH_3\cdot CO_2Et + NaOEt \longrightarrow CH_3\cdot C(OEt)_2\cdot ONa \longrightarrow CH_2:C(OEt)\cdot ONa + EtOH$. $CH_2:C(OEt)\cdot ONa + CH_3\cdot CO_2Et \longrightarrow CH_3\cdot C(OEt)(ONa)\cdot CH_2\cdot CO_2Et \longrightarrow CH_3\cdot C(ONa):CH\cdot CO_2Et + EtOH$. Experiments have proved that this reaction proceeds with measurable velocity at 20°, and that equilibrium is not reached until after about twenty-five days. Meyer and Friessner (Abstr., 1902, i, 657) have found that at 100° equilibrium is attained in two hours.

Michael's conclusion (Abstr., 1901, i, 123; 1905, i, 506) that metallic sodium reacts directly with ethyl acetate with formation of hydrogen and ethyl sodioacetoacetate is untenable for the following reasons. (1) When ethyl acetate in dry ether is treated with sodium, neither hydrogen nor ethyl sodioacetoacetate is produced, but the reaction proceeds thus:

$$2CH_3\cdot CO_2Et + 4Na \longrightarrow ONa\cdot CMe:C(ONa)\cdot CH_3 + 2NaOEt.$$

On treating the product with dilute acid, dimethylketol,

$$OH\cdot CHMe\cdot CO\cdot CH_3,$$

is produced. Acetyldimethylketol *semicarbazone*, m. p. 162°, forms white needles. (2) Ethyl butyrate and ethyl hexoate react with sodium with production of nearly quantitative yields of ketol derivatives of the type $ONa\cdot CR\colon CR\cdot ONa$ (Bouveault and Locquin, Abstr., 1905, i, 560). (3) Propionyl, butyryl, and *iso*valeryl chlorides, on treatment with sodium, yield compounds of the butyroin type, $OH\cdot CHPr^{\alpha}\cdot COPr^{\alpha}$ (Klinger and Schmitz, Abstr., 1891, 890).

By the action of sodium ethoxide on acetethylanilide at 100° in a sealed tube, ethyl acetoacetate was obtained in a yield of 37% of the theoretical. When dry sodium benzyloxide is heated at 180°, various products are obtained, but the main reaction evidently consists in the conversion of the compound into benzoic acid and hydrogen. By the oxidation of sodium benzyloxide in dry air, sodium benzoate and sodium peroxide are produced.

A study was made of the behaviour of sodium benzyloxide towards benzyl acetate, acetethylanilide, formethylanilide, and benzyl sodioacetoacetate under various conditions. In the alkylation of benzyl acetate by sodium benzyloxide, only a 2% yield of benzyl acetoacetate was obtained, whilst in the reaction between ethyl acetate and sodium ethoxide, 36·5% of ethyl sodioacetoacetate is produced when the equilibrium point is reached. Conrad and Hodgkinson (Abstr., 1877, i, 590) found that when benzyl acetate is treated with sodium, benzyl acetoacetate is not formed, but that at 135° hydrogen is evolved and benzyl β-phenylpropionate produced. Bacon (Abstr., 1905, i, 204) has shown that benzyl ether is also produced in this reaction. Experiments have been carried out with a view to ascertain whether the production of the benzyl β-phenylpropionate takes place through an intermediate formation of benzyl acetoacetate, or whether it is due to a direct alkylation of the benzyl acetate by phenylmethylene, thus, $CHPh{<} + H\cdot CH_2\cdot CO_2\cdot C_7H_7 \longrightarrow CH_2Ph\cdot CH_2\cdot CO_2\cdot C_7H_7$. The results show that the alkylation takes place directly without intermediate formation of the acetoacetate, and the same has been found true of the alkylation of benzyl propionate and butyrate. The *copper* derivative of benzyl acetoacetate, m. p. 156°, forms green, feathery crystals.

E. G.

Hydrolysis of Esters of Polyacid Alcohols. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1907, 13, 186—190).—The rate of hydrolysis of glycol monoacetate dissolved in 0·01 and 0·02 *N*-hydrochloric acid at 25·2° is measured. The reaction is of the first order, the velocity constants being $2{\cdot}85 \times 10^{-3}$ and $5{\cdot}65 \times 10^{-3}$. The diacetate is also studied in the same way. In this case the hydrolysis takes place in two stages, $C_2H_4(OAc)_2 + H_2O = OH\cdot C_2H_4\cdot OAc + C_2H_4O_2$ and

$$OH\cdot C_2H_4\cdot OAc + H_2O = C_2H_4(OH)_2 + C_2H_4O_2.$$

The velocity constant of the second reaction being known, it is possible to calculate that of the first from measurements of the rate of hydrolysis of the diacetate. The values of the constant found are $5{\cdot}72 \times 10^{-3}$ in 0·01*N* hydrochloric acid and $9{\cdot}78 \times 10^{-3}$ in 0·02*N* acid.

T. E.

Synthesis of Fats. I. Symmetrical Glycerides. ADOLF GRÜN and P. SCHACHT (*Ber.*, 1907, 40, 1778—1791. Compare Abstr., 1905, i, 562).—The yield of diglyceride obtained by the action of glyceryl disulphate on a fatty acid decreases as the molecular weight of the acid diminishes. Triglycerides of the type β-lauro-α-distearin, obtained by the action of an acid anhydride or chloride on the diglyceride, exist in two forms (compare Duffy, *Jahresb.*, 1852, 507). The one form dissolves readily and has a low m. p., whereas the other is sparingly soluble, and has either a higher m. p. or a double m. p. The glycerides of low m. p. can be crystallised from various solvents without undergoing transformation, but when such a solution is impregnated with a crystal of higher m. p., molecular transformation into the latter form occurs. The reverse change has not been accomplished so far. When melted and solidified, the compounds with double m. p. melt quite sharply at a fixed temperature. Laurodistearin and myristodilaurin give the higher m. p. and myristodistearin and oleodistearin the lower m. p. In the latter cases, however, the compounds after recrystallisation again have two melting points (compare Kreis and Hafner, Abstr., 1903, ii, 190).

Barium glyceroldisulphate, $OH\cdot C_3H_5(O\cdot SO_3)_2Ba,2H_2O$, crystallises from dilute alcohol. The *potassium* salt is anhydrous and sparingly soluble. *β-Aceto-a-distearin*, $OAc\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2$, obtained by heating distearin with an excess of acetic anhydride, forms colourless crystals, m. p. 56·5°; it is sparingly soluble in alcohol and is not decomposed when exposed to bright light for some months in a vacuum.

β-Oleo-a-distearin (Kreis and Hafner, Abstr., 1903, i, 788) melts at 42° when freshly prepared, but after a year has the double m. p. 41° and 55°, and after solidifying melts again at 42°.

β-Lauro-a-distearin, $C_{51}H_{98}O_6$, exists in two forms, which can be separated by some 30—35 crystallisations from ether. The labile form has m. p. 53·5° when freshly prepared and 52·5° after solidifying. The stable form, after crystallising, melts at 56·5° and 68·5°, but after solidifying it has a single m. p. 66·5°.

β-Myristo-a-distearin, $C_{53}H_{102}O_6$, exists in two forms. The labile compound has m. p. 57° when freshly prepared and 55·5° after solidifying. The stable form crystallises in slender, glistening needles practically insoluble in alcohol, m. p. 58·5° and 65°, and after solidifying, 58·5°.

Dimyristin, $C_{31}H_{60}O_5$, forms colourless crystals sparingly soluble in light petroleum, m. p. (from ether) 63°, (from amyl alcohol) 65°. It yields an additive *compound* with myristic acid,

$$OH\cdot C_3H_5(O\cdot CO\cdot C_{13}H_{27})_2,2C_{13}H_{27}\cdot CO_2H,$$

in the form of colourless crystals, m. p. 53·5° or 55°, which are more readily soluble than dimyristin in all organic solvents. *β-Aceto-a-dimyristin*, $C_{33}H_{62}O_6$, crystallises from ether partly in the form of glistening needles, m. p. 41·5°, and partly as nodular masses, m. p. 46·5°. The needles, when kept for some months, also melt at 46·5°.

β-Lauro-a-dimyristin, $C_{43}H_{82}O_6$, forms a microcrystalline powder, m. p. 46·5°, and also exists in a second form, m. p. 36·5°.

Dilaurin, $C_{27}H_{52}O_5$, has been obtained in a liquid form only from glyceroldisulphuric acid, but from a-dichlorohydrin and potassium laurate in the form of nodular masses of needles, m. p. 55°.

β-Myristodilaurin, $C_{41}H_{78}O_6$, exists in two forms, a labile compound crystallising in colourless plates, m. p. 32°, and a stable, microcrystalline powder, m. p. 39·5° (indefinite). An oily laurodimyristin is formed in the preparation of the two β-myristodilaurins.

β *Stearodilaurin*, $C_{45}H_{86}O_5$, has m. p. 37·5° and, after solidifying, 42·5°, and is accompanied by *a-lauro-aβ-distearin*, $C_{51}H_{98}O_6$, which has m. p. 52·5° and, after being kept for some time, 49·5°. J. J. S.

Synthesis of Fats. II. Unsymmetrical Glycerides and their Decomposition. ADOLF GRÜN and E. THEIMER (*Ber.*, 1907, **40**, 1792—1801. Compare preceding abstract).—Unsymmetrical diacyl derivatives of glycerol a-monochlorohydrin of the type $CH_2Cl\cdot CH(OCOR)\cdot CH_2\cdot O\cdot COR$ have been prepared by the action of fatty acids on the disulphate of the monochlorohydrin. As a rule they are accompanied by small amounts of *s*-diglycerides.

a-Chloro-aβ-distearin, $C_8H_5Cl(O\cdot CO\cdot C_{17}H_{35})_2$, crystallises from ether or alcohol and has m. p. 56°, or after solidifying, 41°. The chlorine is not readily replaced by hydroxyl, but when heated with silver nitrite at 120° in a current of hydrogen it yields β-distearin, m. p. 78·2°.

a-Aceto-aβ-distearin, $C_{41}H_{78}O_6$, has m. p. 43°, but after several weeks this has risen to 48°, but after resolidifying has again fallen to 43°.

a-Lauro-aβ-distearin, $C_{51}H_{98}O_6$, has m. p. 49°, or after solidifying, 47°. *a-Myristo-aβ-distearin*, $C_{63}H_{102}O_6$, crystallises from alcohol in short needles, m. p. 52° and 62°, or after solidifying, 59°.

a-Chloro-aβ-dimyristin, $C_3H_5Cl(O\cdot CO\cdot C_{13}H_{27})_2$, forms colourless crystals, m. p. 27—29°. The pure compound, m. p. 29°, is most readily prepared by the action of thionyl chloride on *aβ-dimyristin*, $C_{31}H_{60}O_5$, which melts at 64·5°, or when kept for some months at 62·5°. The isomeric *aa*-dimyristin has m. p. 55° and 61°, or after solidifying, 61°. *a-Lauro-aβ-dimyristin*, $C_{43}H_{82}O_6$, crystallises in needles from alcohol and has m. p. 45°, or after some weeks, 43·5°. *a-Chloro-aβ-dilaurin*, $C_3H_5Cl(O\cdot CO\cdot C_{11}H_{28})_2$, has m. p. 24°. *a-Myristo-aβ-dilaurin*, $C_{41}H_{78}O_6$, has m. p. 41°, or after solidifying, 36·5°. *a-Stearo-aβ-dilaurin*, $C_{45}H_{86}O_6$, has m. p. 46°, or after solidifying, 44°.

a-Chloro-*aβ*-distearin can be progressively hydrolysed by heating it for two hours at 70° with 10 mols. of 98% sulphuric acid. The products are stearic acid, monostearin, and monostearochlorohydrin.

J. J. S.

Theory of Saponification. III. MILAN J. STRITAR and RICHARD FANTO (*Monatsh.*, 1907, **28**, 383—396. Compare Abstr., 1904, i, 843; this vol., i, 277; Kremann, Abstr., 1905, ii, 630; 1906, ii, 731).—This is in part a reply to Kremann (*loc. cit.*) and Lewkowitsch (this vol., i, 10). The authors' view that the saponification of glycerides by means of alcoholic alkalis takes place chiefly by direct hydrolysis of the triglyceride, the displacement of the glycerol by the solvent alcohol and subsequent hydrolysis of the ester so formed being minor reactions, is in opposition to that of Kremann, according to which direct hydrolysis of the triglyceride does not take place. Whilst the displacement of the glycerol is almost instantaneous in presence of much alkali, if the amount of the latter is limited the reaction takes place much more slowly and can be followed quantitatively, in the case of triacetin when about 3% of the alkali required for total saponification is employed, or in that of rape-seed oil when the amount of alkali present has diminished from 16% to 7%.

A number of experiments with rape-seed oil, in which the hydrolysis was stopped by addition of a known amount of acetic acid in the manner previously described (this vol., i, 277), the excess of acetic acid titrated, the soap decomposed by acetic acid, and the alcohol and glycerol determined in the washed and dried fat, are described and the results tabulated. It is found that the sum of the hydroxyl ions consumed (s) and the hydroxyl equivalents of the alcohol (a) and of the glycerol (g) found is greater than the ester number (e) of the original, neutral fat. One at least of the two reactions, direct hydrolysis of the triglyceride and displacement of the glycerol, must take place in more than one stage, since if both reactions were to take place directly, $s + a + g$ must equal e. An approximate calculation of the composition of the residue shows that the amount of ester formed is 36—37% in excess of that required by the direct reaction. The amount of glycerol found points to the presence of a diacin. It is argued that the reaction taking place in more than one stage is the displacement of the glycerol.

Further light can be thrown on the course of the saponification only by isolation of the intermediate products, which will be attempted.

G. Y.

Reagent in the Chemistry of Fats. II. ERNEST TWITCHELL (*J. Amer. Chem. Soc.*, 1907, **29**, 566—571. Compare Abstr., 1906, i, 331).—In the earlier paper it was pointed out that sulphophenyl- and sulphonaphthyl-stearic acids act as catalytic agents in the hydrolysis of fats. It is now found that these acids are also capable of accelerating the esterification of the higher fatty acids under conditions in which the process would otherwise be scarcely noticeable. The reaction only takes place completely when the water produced is removed; the use of these sulphostearic acids is therefore especially applicable to the esterification of the higher fatty acids and alcohols which are not readily volatile at 100°, since the action occurs rapidly at this temperature and the water can be eliminated by evaporation.

Experiments are described in which the quantitative esterification of glycerol and other alcohols by commercial stearic acid (a mixture of stearic and palmitic acids) has been effected by means of sulphonaphthylstearic acid. From the results obtained, the "hydroxyl value" (milligrams of potassium hydroxide containing the same amount of hydroxyl as 1 gram of the alcohol) of the alcohols has been calculated. The reaction has been extended to the estimation of the alcoholic hydroxyl value of hydroxy-acids of the fatty series and their glycerides. The following hydroxyl values have been obtained: lard, 1·8; fatty acids of lard, 8·3; tallow fatty acids, 2·3; olive oil, 6·4 and 5·0; cotton-seed oil, 7·8 and 8·2; fatty acids of cotton-seed oil, 12·8; castor oil, 149·0; and fatty acids of castor oil, 161·4.

Experiments have also been made which show that the higher fatty acids can be quantitatively esterified by alcohols, such as glycerol, ceryl alcohol, and amyl alcohol, in presence of sulphonaphthylstearic acid.

E. G.

Optical Activity of Mineral Oil. Julius Marcusson (*Chem. Zeit.*, 1907, 31, 419—422).—On fractionally distilling the unsaponifiable portion of an olein, obtained from tallow and palm fat, it was found that the rotatory power of the fractions increased as their boiling points rose. This is in agreement with Engler's observations on mineral oil. Determinations of the iodine number of the various fractions gave widely different results, according as they were made by the Wys or Hübl-Waller method. This phenomenon is also exhibited by cholesterol, but not by ordinary fats. A further point of resemblance between artificial and natural mineral oils lay in the fact that the optical activity of both is diminished by concentrated sulphuric acid. In reply to Neuberg's objection (Abstr., 1906, i, 923) that the amount of cholesterol in fat is too small to account for the high optical activity of some mineral oils, it is pointed out that the fats of marine animals, which, according to Engler, probably form the chief source of these oils, contain a much larger percentage of cholesterol than ordinary fat, and that, moreover, cholesterol or phytosterol form normal constituents of almost every part of the animal or vegetable organism. The author also criticises the theories of Neuberg and Walden. P. H.

Diacetylcarboxylic Acid. Carl D. Harries and Karl Kircher (*Ber.*, 1907, 40, 1651—1652).—*Diacetylcarboxylic acid*, $CH_3\cdot CO\cdot CO\cdot CH_2\cdot CO_2H$, is obtained as a yellow, viscous oil by treating a chloroform solution of β-benzylidenelævulic acid with ozone and decomposing the product with water. It is stable to boiling water, and forms a green *copper* salt, $C_{10}H_{10}O_8Cu$. The *bisphenylhydrazone*, $C_{17}H_{18}O_2N_4$, m. p. 175°, forms yellow prisms, and the *bis-semicarbazone* a white powder, m. p. 240°. The *ethyl* ester, $CH_3\cdot CO\cdot CO\cdot CH_2\cdot CO_2Et$, has b. p. 79—80·5°/10 mm., and its *phenylhydrazone* has m. p. 115°. C. S.

Condensation of Ethyl Oxalate with Dimethylketol. Otto Diels and Max Stern (*Ber.*, 1907, 40, 1622—1629).—The work of Diels and Plant (Abstr., 1905, i, 509) has been continued with the view of utilising 1 : 2-diketones for the synthesis of cyclic polyketones.

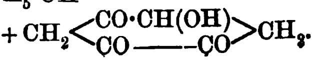
Diacetylmonoxime methyl ether, $COMe\cdot CMe\colon N\cdot OMe$, is readily obtained by the action of methyl sulphate on diacetylmonoxime, and, when condensed with ethyl oxalate, forms the *compound*, $CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CMe\colon N\cdot OMe$, which separates from acetone in felted needles, m. p. 88°. The *acid* has m. p. 114°. Attempts to convert these substances into cyclic compounds by elimination of alcohol or water failed.

The *compound*, $CHPh\colon CH\cdot CO\cdot CMe\colon N\cdot OMe$, obtained by condensing diacetylmonoxime methyl ether with benzaldehyde, crystallises in prisms, m. p. 82°, and has b. p. 165—167°/14 mm.

When dimethylketol is condensed with ethyl oxalate, the actions, represented by the following equations, probably take place:

$$(1)\ CO_2Et\cdot CO_2Et + CH_3\cdot CO\cdot CH(OH)\cdot CH_3 = C_2H_5\cdot OH + CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CH(OH)\cdot CH_3;$$

$$(2)\ CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CH(OH)\cdot CH_3 = C_2H_5\cdot OH$$



$$+ CH_2{<}\begin{matrix}CO\cdot CH(OH)\\ CO\text{———}CO\end{matrix}{>}CH_2.$$

The resulting *compound*, $C_6H_6O_4$, is acid in character, and can be titrated like a monobasic acid. With phenylhydrazine, it forms a *dihydrazone*, $C_{18}H_{18}O_2N_4$, with m. p. 114·5° (decomp.); when methylated with diazomethane it forms a *methyl* derivative, $C_7H_8O_4$, which separates from alcohol in glistening leaflets, m. p. 91°, and which reduces Fehling's solution.

The compound, $C_6H_6O_4$, combines with *o*-phenylenediamine to form a characteristic *quinoxaline* derivative, $C_{12}H_{12}O_3N_2$, which forms bright red needles, m. p. 237° (decomp.). A. McK.

Double Cobalt Malonates. RICHARD C. LORD (*J. Physical Chem.*, 1907, **11**, 173—200).—Cobalt malonate and a series of double cobalt malonates have been prepared. Denoting the malonic acid radicle by *M*, the composition of these is represented by the following formulæ. In most cases the specific gravity has been determined, this being indicated by the figures in brackets. $CoM,2H_2O$ (2·279), $H_2CoM_2,2H_2O$, $(NH_4)_2CoM_2,4H_2O$ (1·804), $K_2CoM_2,4H_2O$ (2·234), $Rb_2CoM_2,4H_2O$ (2·131), $Cs_2CoM_2,4H_2O$ (2·682), K_2CoM_2.

Solubility measurements at 18° gave the following numbers, which express the number of grams of anhydrous salt in 100 grams of solution: CoM, 1·353; $(NH_4)_2CoM_2$, 10·61; K_2CoM_2, 4·26; Cs_2CoM_2, 14·23.

The electrical conductivity of the solutions of the double cobalt malonates is very much smaller than the sum of the conductivities of corresponding solutions of cobalt malonate and the alkali malonates. The difference between these values also increases considerably with the dilution. From this, in conjunction with the fact that the addition of an alkali malonate to a solution of cobalt malonate causes a change in colour from a bright red to a purple-red, the conclusion is drawn that the double cobalt malonates are in reality complex salts, which dissociate electrolytically with the formation of complex cobalt malonyl ions of considerable stability. Migration experiments are described which support this conclusion. On electrolysing solutions of the complex cobalt malonates, acidified with malonic acid, the colour of the anode solution changes to green. The author supposes that cobaltimalonates are formed in these circumstances, but attempts to separate crystalline malonates containing tervalent cobalt were unsuccessful. H. M. D.

Esterification of Succinic Acid. ISAAC K. PHELPS and J. L. HUBBARD (*Amer. J. Sci.*, 1907, **23**, 368—374).—It was shown (this vol., ii, 297) that pure succinic acid is obtained best by hydrolysis of ethyl succinate; in the present paper the preparation of the pure ester, and the conditions under which its formation takes place almost quantitatively, are described.

The results of a number of experiments show that whilst the yield of ethyl succinate depends to some extent on the purity of the succinic acid and the alcohol employed, on the proportion of hydrogen chloride (compare Fischer and Speier, Abstr., 1896, i, 201), and the time of the reaction, it is affected to a more considerable extent by the removal of the water formed during the esterification. This is accomplished by passing alcohol vapour charged with hydrogen chloride into a mixture of succinic acid, alcohol, and hydrogen chloride, distilling continuously at 100—110°. In this manner, a 97% yield of ethyl succinate is obtained from 50 grams of succinic acid in five hours, whilst the yield may be increased to 97·7% in two and a half hours if after one and a half hours the whole of the alcohol, water, and hydrogen chloride in the distilling flask is removed by distillation at 60°/15 mm. and the esterification process repeated. Only small amounts of ethyl succinate are found in the alcoholic-acid distillate. G. Y.

Ester-, Amide-, Anilide-, and *p*-Toluidide-Acids of Mesaconic Acid. RICHARD ANSCHÜTZ [and, in part, JULIEN DRUGMAN, FERDINAND HAAS, OSWALD SCHARFENBERG, and OTTO SIEPLEIN] (*Annalen*, 1907, **343**, 139—208. Compare Abstr., 1890, 368; 1898, i, 128; Cloëz, Abstr., 1890, 739).—Hydrogen β-ethyl mesaconate,

$$CO_2H\cdot CH{:}CMe\cdot CO_2Et,$$

m. p. 67—68°, was prepared by Cloëz (*loc. cit.*) by the action of barium carbonate and water on ethyl dibromomethylacetoacetate. On partial esterification of mesaconic acid, Anschütz and Drugman (Abstr., 1898, i, 128) obtained a hydrogen ethyl mesaconate, m. p. 42°, which they considered to be the α-ethyl ester, $CO_2Et\cdot CH{:}CMe\cdot CO_2H$, and, by partial hydrolysis of ethyl mesaconate, a hydrogen ethyl mesaconate, m. p. 67—68°, which they assumed to be identical with Cloëz's β-ethyl ester. Certain observations made in the preparation of mesaconamic and mesaconanilic acids having thrown doubt on the constitution of Anschütz and Drugman's esters, the partial hydrolysis of methyl mesaconate and partial methylation of mesaconic acid have been studied. It is found that whilst the product of the partial hydrolysis is almost pure hydrogen α-methyl mesaconate, that of the partial methylation is a mixture of the α- and β-methyl esters. The reinvestigation of the hydrogen ethyl esters led to similar results; the ester-acid obtained by partial hydrolysis of ethyl mesaconate is hydrogen α-ethyl mesaconate and is isomeric with Cloëz's hydrogen β-ethyl ester which melts at the same temperature, whilst the product of the partial esterification is a mixture of the α- and β-ethyl esters.

In the experimental part of the paper, the formation of these ester-acids and of the corresponding mesaconamic, mesaconanilic, and mesacon-*p*-toluidic acids, by conversion into which the ester-acids have been separated and identified, is described. It is shown that the α-alkyl esters, which are formed by partial hydrolysis, are the main components of the mixtures obtained by partial esterification, from which it is concluded that the alkyl, which is the more difficult to introduce, is the first removed by hydrolysis.

The action of limited amounts of aniline and *p*-toluidine on mesaconyl chloride leads to the formation of almost pure mesaconanilyl and mesacon-*p*-toluidyl chlorides respectively, the chlorine of the more acid α-carboxyl chloride group reacting more readily with bases than that of the β-carboxyl chloride.

Hydrogen α-methyl mesaconate, m. p. 52°, has the solubility 12·07/100 aq. at 20°, and the conductivity constant $K = 0{\cdot}0353$; the *silver* salt was analysed; the *ammonium* salt, m. p. 153—154°. Hydrogen β-methyl mesaconate crystallises from light petroleum in small needles, m. p. 84°, b. p. 135—137°/13 mm., and has the solubility 2·55/100 aq. at 20°, and the conductivity constant $K=0{\cdot}051$; the *silver* and *ammonium*, m. p. 144—146°, salts were analysed. The mixture of α- and β-methyl esters formed by partial esterification, m. p. 36—46°.

Hydrogen α-ethyl mesaconate crystallises from benzene in needles, m. p. 67—68°, b. p. 141·6—142·2°/14 mm., and has the solubility 1·91/100 aq. at 20°, and the conductivity constant $K=0{\cdot}0342$; the *ammonium* salt, m. p. 127—128°; the *silver* salt was analysed. Hydrogen β-ethyl mesaconate crystallises from light petroleum in small, white needles, m. p. 68°, is odourless when pure, and has the solubility 1·49/100 aq. at 20°, and the conductivity constant $K=0{\cdot}0553$; the *silver* and *ammonium*, m. p. 102—103°, salts were analysed. A mixture of equal parts of the α- and β-ethyl esters, m. p. 46—52°, whilst that, m. p. 42—45°, formed by partial esterification of mesaconic acid, contains 60% of the α-ethyl ester. Mixtures of the α- and β-esters are obtained also by heating ethyl mesaconate with mesaconic acid.

When treated with phosphorus pentachloride in chloroform solution and distilled, the mixture of hydrogen methyl mesaconates, obtained by esterification, yields a mixture of methyl mesaconyl chlorides, b. p. 79·2°/12 mm., D_4^{15} 1·228, and a mixture of the methyl-ester anhydrides, b. p. 196°/14 mm. The individual ester-chlorides and ester-anhydrides are obtained by the action of phosphorus pentachloride on the pure hydrogen methyl and hydrogen ethyl esters. *α-Methyl mesaconyl β-chloride*, $CO_2Me{\cdot}CH{:}CMe{\cdot}COCl$, b. p. 80°/13 mm., D_4^{15} 1·224. *β-Methyl mesaconyl α-chloride*, $COCl{\cdot}CH{:}CMe{\cdot}CO_2Me$, b. p. 79—80°/13 mm. or 92—93°/20 mm., D_{20}^{20} 1·232. *α-Ethyl mesaconyl β-chloride*, $C_7H_9O_3Cl$, b. p. 86—87°/13 mm., D_{20}^{20} 1·173. *β-Ethyl mesaconyl α-chloride*, b. p. 88—90°/13 mm., D_{20}^{20} 1·184. These ester-chlorides are hydrolysed by water, forming the corresponding hydrogen alkyl mesaconates from which they are obtained.

α-Methyl mesaconic anhydride, $O(CO{\cdot}CMe{:}CH{\cdot}CO_2Me)_2$, b. p. 190—195°/13 mm., D_{20}^{20} 1·232. *β-Methyl mesaconic anhydride*, a yellow oil, b. p. 190—195°/13 mm., D_{20}^{20} 1·263. *α-Ethyl mesaconic anhydride*, b. p. 202—203°/13 mm., D_{20}^{20} 1·159. *β-Ethyl mesaconic anhydride*,

$$O(CO{\cdot}CH{:}CMe{\cdot}CO_2Et)_2,$$

b. p. 200—205°/14 mm., D_{20}^{20} 1·187. When treated with ammonia in ethereal solution these ester-anhydrides form the corresponding ammonium alkyl mesaconates and alkyl mesaconamates.

β-Methyl α-ethyl mesaconate, $CO_2Et{\cdot}CH{:}CMe{\cdot}CO_2Me$, formed by the action of methyl iodide on silver α-ethyl mesaconate, b. p. 95·2—95·6°/12 mm., D_{20}^{20} 1·079, yields hydrogen α-ethyl mesaconate on partial hydrolysis. *α-Methyl β-ethyl mesaconate*,

$$CO_2Me{\cdot}CH{:}CMe{\cdot}CO_2Et,$$

b. p. 97—98°/13 mm., D_{20}^{20} 1·076.

α-Methyl mesacon-β-amate, $CO_2Me{\cdot}CH{:}CMe{\cdot}CO{\cdot}NH_2$, formed by the action of ammonia on the α-methyl ester-chloride or of methyl iodide on silver mesacon-β-amate, crystallises in needles, m. p. 103°, and is converted by nitrous acid into hydrogen α-methyl mesaconate.

α-Ethyl mesacon-β-amate, $CO_2Et\cdot CH\colon CMe\cdot CO\cdot NH_2$, crystallises in small, tetragonal prisms, m. p. 78°. *Mesacon-β-amic acid*,

$$CO_2H\cdot CH\colon CMe\cdot CO\cdot NH_2,$$

m. p. 174°, is formed by hydrolysis of its esters with potassium hydroxide at the ordinary temperature; the *ammonium*, m. p. 144—146°, and *silver* salts are described.

β-Methyl mesacon-α-amate, $NH_2\cdot CO\cdot CH\colon CMe\cdot CO_2Me$, m. p. 117°. *β-Ethyl mesacon-α-amate* forms small, hard crystals, m. p. 96°. *Mesacon-α-amic acid*, $NH_2\cdot CO\cdot CH\colon CMe\cdot CO_2H$, m. p. 222°; the *ammonium*, m. p. 183—184°, and *silver* salts are described.

Mesaconanilic and mesacon-*p*-toluidic esters are formed by the action of aniline and *p*-toluidine respectively on the ester-chlorides, or of alkyl iodides on the silver mesaconanilates and *p*-toluidates. The anilic and *p*-toluidic acids are obtained by hydrolysis of their esters with the calculated amount of potassium hydroxide at the ordinary temperature. The mesaconanilic acids, obtained from the product of the partial methylation of mesaconic acid, can be separated by fractional crystallisation from water.

Mesacon-β-anilic acid, $CO_2H\cdot CH\colon CMe\cdot CO\cdot NHPh$, crystallises in glistening leaflets, m. p. 163°, is readily soluble in hot water, and when heated with an excess of potassium hydroxide at 100° yields aniline and mesaconic acid; the *silver* salt was analysed. *α-Methyl mesacon-β anilate*, m. p. 91—92°. *α-Ethyl mesacon-β-anilate* crystallises in needles, m. p. 72°.

Mesacon-α-anilic acid, $NHPh\cdot CO\cdot CH\colon CMe\cdot CO_2H$, crystallises in microscopic needles, m. p. 202°, is sparingly soluble in hot water, and yields aniline and mesaconic acid when heated with potassium hydroxide at 100°; the *silver* salt was analysed. *β-Methyl mesacon-α-anilate* forms long needles, m. p. 92°; a mixture of this with the α-methyl β-anilate, m. p. 65°. *β-Ethyl mesacon-α-anilate*, m. p. 92°.

*Mesacon-β-*p*-toluidic acid*, $CO_2H\cdot CH\colon CMe\cdot CO\cdot NH\cdot C_7H_7$, crystallises in small needles, m. p. 184°; the *silver* salt was analysed. *α-Methyl mesacon-β-*p*-toluidate*, $C_{13}H_{15}O_3N$, m. p. 105°. *α-Ethyl mesacon-β-*p*-toluidate* crystallises in white needles, m. p. 99°.

*Mesacon-α-*p*-toluidic acid*, $C_7H_7\cdot NH\cdot CO\cdot CH\colon CMe\cdot CO_2H$, white needles, m. p. 196°; the *silver* salt was analysed. The *methyl* ester crystallises from methyl alcohol in needles, or from acetic acid in leaflets, m. p. 135°. The *ethyl* ester, white needles, m. p. 103°.

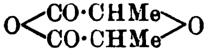
Mesacon-α-anilyl chloride, $NHPh\cdot CO\cdot CH\colon CMe\cdot COCl$, formed by the action of 2 mols. of aniline on mesaconyl chloride in ethereal solution, crystallises from benzene in light yellow needles, m. p. 107°, and yields on hydrolysis mesacon-α-anilic acid, or with methyl alcohol the β-methyl α-anilate. *Mesacon-α-anil-β-amide*,

$$NHPh\cdot CO\cdot CH\colon CMe\cdot CO\cdot NH_2,$$

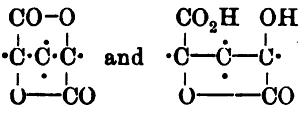
formed by the action of ammonia on the α-anilyl chloride in ethereal solution, crystallises in needles, m. p. 165°. *Mesacon-α-anil-β-*p*-toluidide*, $NHPh\cdot CO\cdot CH\colon CMe\cdot CO\cdot NH\cdot C_7H_7$, from *p*-toluidine and the α-anilyl chloride, crystallises from alcohol in white needles, m. p. 189°.

*Mesacon-α-*p*-toluidyl chloride*, $C_7H_7\cdot NH\cdot CO\cdot CH\colon CMe\cdot COCl$, crystallises in sulphur-yellow needles, m. p. 115°, and yields the corresponding toluidic acid and its esters on treatment with alkalis, or methyl or ethyl alcohol. *Mesacon-a-*p*-toluidide-β-amide*, $C_7H_7\cdot NH\cdot CO\cdot CH{:}CMe\cdot CO\cdot NH_2$, white needles, m. p. 177—178°. *Mesacon-β-anil-a-*p*-toluidide*, $C_7H_7\cdot NH\cdot CO\cdot CH{:}CMe\cdot CO\cdot NHPh$, white needles, m. p. 183°; a mixture of this with its isomeride, m. p. 172—174°. *Mesacon-*p*-toluidide*, $C_7H_7\cdot NH\cdot CO\cdot CH{:}CMe\cdot CO\cdot NH\cdot C_7H_7$, white needles, m. p. 212°.

Pebal's silver hydrogen mesaconate (*Annalen*, 1851, **78**, 139), which, contrary to that author's statement, crystallises from a solution of silver mesaconate in a concentrated, aqueous solution of an excess of mesaconic acid, is the β-silver salt, since on treatment with methyl and ethyl iodides it yields almost pure hydrogen β-methyl and hydrogen β-ethyl mesaconates. The solution of silver mesaconate in an excess of mesaconic acid, before crystallisation of the β-silver salt, contains the a- and β-silver salts in equilibrium, the a-salt preponderating, since the action of ethyl iodide on the solution leads to the formation of a mixture of hydrogen ethyl mesaconates, of which the a-ethyl ester is the chief component. G. Y.

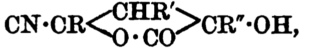
r-Dilactylic Acid. ÉMILE JUNGFLEISCH and MARCEL GODCHOT (*Compt. rend.*, 1907, **144**, 979—981).—The product formed by the action of ethyl a-chloropropionate on the sodium derivative of ethyl lactate is not, as von Brüggen supposed (*Annalen*, 1868, **148**, 224), ethyl ethyl-lactyl-lactate, $OEt\cdot CHMe\cdot CO_2\cdot CHMe\cdot CO_2Et$, but ethyl dilactylate, $O(CHMe\cdot CO_2Et)_2$, b. p. 110—112°/15 mm., D^{20} 1·051, identical with that obtained by Wurtz and Friedel (*Ann. Chem. Pharm.*, 1861, **63**, 114) and Tanatar and Tschelebéeff (Abstr., 1891, 177). The *free acid*, m. p. 106°, crystallises from benzene in lamellæ and from water in prisms, and on distillation, even under reduced pressure, yields *dilactylic anhydride*,  $O<\begin{matrix}CO\cdot CHMe\\CO\cdot CHMe\end{matrix}>O$, b. p. 110°/20 mm., a colourless liquid which, in contact with water, slowly regenerates the acid. T. A. H.

Dilactones. II. RUDOLF FITTIG (*Annalen*, 1907, **353**, 1—64. Compare Abstr., 1901, i, 120).—This investigation has been continued with the object of determining the influence of the position of the lactone rings in the molecule on the chemical properties of the dilactones and of the corresponding hydroxy-lactonic acids. The substances examined are chiefly those containing the annexed groupings. The simplest of these, the dilactone (pentadilactone) and monolactone (pentoxylactonic acid) of aγ-dihydroxyglutaric acid, have been prepared and will be described later; in the present paper, the derivatives of homologues of aγ-dihydroxyglutaric acid, $CO_2H\cdot CR(OH)\cdot CHR'\cdot CR''(OH)\cdot CO_2H$, are described.



The work of Zelinsky on the derivatives of aγ-dihydroxy-aγ-dimethylglutaric acid (Abstr., 1892, 436. Compare Auwers and Kauffmann, Abstr., 1893, i, 72; Michael and Lamb, this vol., i, 134) has been repeated; it is found that that author's supposed stable αγ-dihydroxy-αγ-dimethylglutaric acid is a monobasic hydroxy-lactonic acid, which nullifies the arguments as to the stereo-configuration of the supposed isomeric dihydroxydimethylglutaric acids and their relation to dimethyltartaric acid.

The αγ-dihydroxyglutaric acids are obtained from the corresponding diketones, which, when shaken with cold saturated aqueous potassium cyanide, develop heat and form potassium derivatives yielding the dihydroxy-dinitriles, $\mathrm{OH{\cdot}CR(CN){\cdot}CHR'{\cdot}CR''(CN){\cdot}OH}$, on treatment with carbon dioxide; the potassium derivatives readily decompose, and only one, $\mathrm{OK{\cdot}CMe(CN){\cdot}CH_2{\cdot}CPr^{\alpha}(CN){\cdot}OK}$, has been isolated. The dihydroxy-dinitriles undergo hydrolysis in two stages; the products of the first stage are hydroxylactone-nitriles,

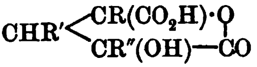


$$\mathrm{CN{\cdot}CR}\Big\langle\begin{matrix}\mathrm{CHR'}\\ \mathrm{O{\cdot}CO}\end{matrix}\Big\rangle\mathrm{CR''{\cdot}OH},$$

which, when boiled with water, lose hydrogen cyanide, forming hydroxy-ketonic acids, $\mathrm{CO_2H{\cdot}CR(OH){\cdot}CHR'{\cdot}COR''}$, or

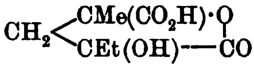
$$\mathrm{COR{\cdot}CHR'{\cdot}CR''(OH){\cdot}CO_2H},$$

but are hydrolysed by concentrated hydrochloric acid at the ordinary temperature, yielding the hydroxy-lactonic acids (I). It is found that with R and R″ = Me, and R′ = H, the hydroxy-lactonic acid, obtained from the nitrile, is not identical with that formed by partial hydrolysis of the dilactone, whereas the same hydroxy-lactonic acid is obtained by both methods if R and R″ are different alkyls and R′ = H; the constitution of the hydroxy-lactonic acid, which may be II or III, has not been determined.



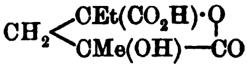
$$\mathrm{CHR'}\Big\langle\begin{matrix}\mathrm{CR(CO_2H){\cdot}O}\\ \mathrm{CR''(OH){-}{-}CO}\end{matrix}$$

(I.)



$$\mathrm{CH_2}\Big\langle\begin{matrix}\mathrm{CMe(CO_2H){\cdot}O}\\ \mathrm{CEt(OH){-}{-}CO}\end{matrix}$$

(II.)



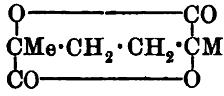
$$\mathrm{CH_2}\Big\langle\begin{matrix}\mathrm{CEt(CO_2H){\cdot}O}\\ \mathrm{CMe(OH){-}{-}CO}\end{matrix}$$

(III.)

The tendency to formation of isomerides is much greater if R′ is an alkyl group, the dinitrile, $\mathrm{OH{\cdot}CMe(CN){\cdot}CHEt{\cdot}CMe(CN){\cdot}OH}$, being obtained in two modifications, one of which behaves as described above, whilst the *iso*-compound, when treated with concentrated hydrochloric acid at the ordinary temperature, forms a hydroxy-lactone-amide which is further hydrolysed by hot concentrated hydrochloric acid, yielding the same acid as is obtained directly from the first modification of the dinitrile.

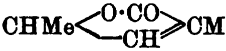
A dihydroxy-dinitrile has been obtained in the same manner from acetonylacetone (Zelinsky and Isaieff, Abstr., 1896, i, 413). On hydrolysis with concentrated hydrochloric acid, it yields a δδ-dilactone and two isomeric dihydroxydicarboxylic acids,

$$\mathrm{CO_2H{\cdot}CMe(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CO_2H}.$$

The δδ-dilactone,  $\begin{matrix}\mathrm{O}&\text{———————}&\mathrm{CO}\\ \mathrm{CMe}&\mathrm{{\cdot}CH_2{\cdot}CH_2{\cdot}}&\mathrm{CMe}\\ \mathrm{CO}&\text{———————}&\mathrm{O}\end{matrix}$, is more stable than the γγ-dilactones described above.

Derivatives of αγ-dihydroxy-αγ-dimethylglutaric acid.—[With **Paul**

Kraus.]—The *calcium*, *barium* ($3H_2O$), and *silver*, $C_7H_9O_5Ag$, salts of the hydroxylactone acid, m. p. 186°, are described. The barium, $C_7H_{10}O_6Ba$, and *calcium* ($\frac{1}{2}H_2O$) salts of the dibasic acid were analysed; on liberation from its salts, the dibasic acid changes into the hydroxy-lactonic acid, m. p. 186°. The *iso*hydroxy-lactonic acid, $C_7H_{10}O_5,H_2O$, formed by the action of water on the dilactone, is identical with Zelinsky's dihydroxydimethylglutaric acid, loses H_2O at 95—100°, and when anhydrous crystallises from ether in prisms, m. p. 107°; the *calcium* ($9H_2O$), *barium* (H_2O), and *silver*, $C_7H_9O_5Ag$, salts are described.

a-Methylpentenolactone,  $\mathrm{CHMe}\!<\!\begin{matrix}\mathrm{O\cdot CO}\\ \mathrm{CH}\end{matrix}\!>\!\mathrm{CMe}$, is formed, together with the dilactone, by distillation of the hydroxy-lactonic acid, as an oil, b. p. 205—207°, and, with bases, forms salts of *a*-methyllævulic acid. The *calcium* and *barium* salts and the *phenylhydrazone*, $C_{12}H_{17}O_2N_2$, white needles, decomposing on exposure to air, are described.

(Béhal, Abstr., 1901, i, 278, obtained a lactone, b. p. 205—206°, by distilling *a*-methyllævulic acid.)

Derivatives of aγ-dihydroxy-a-methyl-γ-ethyl- and aγ-dihydroxy-a-methyl-γ-n-propyl-glutaric acids.—[With Joseph von Panayeff.]—The *dihydroxy-dinitrile*, R = Me, R′ = H, R″ = Et, prepared from propionylacetone, crystallises from a mixture of alcohol and ether in small leaflets, m. p. 145° (decomp.). The *hydroxy-lactonic nitrile*, $C_8H_{11}O_3N$, crystallises in monoclinic prisms, m. p. 114°, distils at the ordinary temperature with slight decomposition, and when boiled with water yields the *keto-acid*, $C_7H_{12}O_4$. This is obtained as a viscid liquid, b. p. 160—165°/100 mm.; the *calcium* salt, $(C_7H_{11}O_4)_2Ca,H_2O$, was analysed; the *phenylhydrazone*, $C_{13}H_{18}O_3N_2$, crystallises in colourless plates, m. p. 121° (decomp.). The *hydroxy-lactonic acid*, $C_8H_{12}O_5,H_2O$, crystallises in rhombic plates, m. p. 84°, or, when anhydrous, forms small, flat crystals, m. p. 122°; the *calcium* and *silver* salts were analysed. The *calcium*, $C_8H_{12}O_6Ca,6H_2O$, and *silver* salts of aγ-dihydroxy-*a*-methyl-γ-ethylglutaric acid are described. The *dilactone*, $C_8H_{10}O_4$, crystallises in small leaflets, m. p. 55°, and yields the hydroxy-lactonic acid on recrystallisation from water.

The *potassium* derivative of the dinitrile of *a*γ-dihydroxy-*a*-methyl-γ-*n*-propylglutaric acid, $C_9H_{12}O_2N_2K_2$, crystallises in nacreous leaflets, decomposes on exposure to air, losing hydrogen cyanide, and blues moistened, red litmus paper. The *dinitrile*, $C_9H_{14}O_2N_2$, crystallises in prisms, m. p. 137° (decomp.) The *hydroxy-lactonic nitrile*, $C_9H_{13}O_3N$, forms monoclinic prisms, m. p. 125°.

Derivatives of aγ-dihydroxy-aγ-dimethyl-β-ethylglutaric acid.—[With Walter Peters.]—The action of potassium cyanide on ethylacetylacetone leads to the formation of two products which are separated by recrystallisation from ether or chloroform. The dihydroxydinitrile, $C_9H_{14}O_2N_2$, crystallises in small, monoclinic plates, m. p. 139° (decomp.). The iso-*compound* crystallises in thin, tetragonal needles, m. p. 124° (decomp.), and is more soluble in ether or chloroform than its isomeride. The *hydroxy-lactonic nitrile*, $C_9H_{13}O_3N$, crystallises in rhombic plates [$a:b:c = 0{\cdot}8760:1:0{\cdot}8103$], m. p. 109°, has piezoelectrical properties when powdered, is decomposed by boiling water, and when treated with cold concentrated hydrochloric acid is gradually converted into the *hydroxy-lactonic acid*, $C_9H_{14}O_5$, which crystallises in prisms, m. p. 140°, and is hygroscopic; the *calcium*, $(C_9H_{13}O_5)_2Ca$, *barium*, and *silver* salts were analysed. The iso*hydroxy-lactonic nitrile*, $C_9H_{13}O_3N$, formed from the *iso*dinitrile, crystallises in monoclinic or triclinic plates, m. p. 72°, and is converted by cold concentrated hydrochloric acid into the corresponding *amide*, $C_9H_{15}O_4N$, which crystallises in rhombic plates, m. p. 223°, sublimes above 250°, and on hydrolysis with alkalis or hot hydrochloric acid yields the hydroxy-lactonic acid, m. p. 140°. The *barium*, $C_9H_{14}O_6Ba$, and *calcium* salts of dihydroxydimethylethylglutaric acid were analysed. The *dilactone*, $C_9H_{12}O_4$, crystallises from light petroleum in rhombohedra, m. p. 52°, and when shaken with cold water gradually forms the hydroxy-lactonic acid.

Derivatives of αδ-dihydroxy-αδ-dimethyladipic acid.—[With FRITZ LENTZ.]—The *dinitrile*, formed by the action of potassium cyanide on acetonylacetone, was not isolated. αδ-Dihydroxy-αδ-dimethyladipic acid, $C_8H_{14}O_6$, crystallises in monoclinic prisms, m. p. 206—208°; the *calcium* ($6H_2O$), *barium* ($5H_2O$), and *silver* salts were analysed. When heated at 160°, the dihydroxy-acid yields the *hydroxy-lactonic acid*, $C_8H_{12}O_5$, stout crystals, m. p. 139—140°, or on distillation the hydroxy-lactonic acid together with the *dilactone*, $C_8H_{10}O_4$. This separates from ether in large crystals, m. p. 95—96°, sublimes above 100°, and is hydrolysed by boiling water, forming αδ-dihydroxy-αδ-dimethyladipic acid.

iso-*αδ-Dihydroxy-αδ-dimethyladipic acid*, formed in small quantity from the dinitrile, crystallises in needles, m. p. 189° (decomp.); the *calcium* ($5H_2O$) and *barium* ($5H_2O$) salts were analysed. When boiled with water, the *iso*-acid is converted partially into its isomeride, whilst the action of concentrated hydrochloric acid and ether converts it slowly and partially into the dilactone; when distilled the *iso*-acid yields the dilactone, but at 160° is converted into an iso*hydroxy-lactonic acid*, $C_8H_{12}O_5$, which crystallises in leaflets, m. p. 153°, and on recrystallisation from water yields dihydroxydimethyladipic acid. G. Y.

Esters of Orthotrithioformic Acid. BROR HOLMBERG (*Ber.*, 1907, 40, 1740—1743).—Simple mercaptans can be condensed by means of anhydrous hydrogen chloride with derivatives of formic acid to form esters of orthotrithioformic acid of the type $CH(SR)_3$.

Ethyl orthotrithioformate is a colourless oil, b. p. 133°/21 mm., 119°/12 mm., 116°/10 mm., of characteristic, unpleasant odour; D_4^{20} 1·053. Phenyl orthotrithioformate, prepared from phenyl mercaptan and formic acid, m. p. 40°, is identical with that prepared by Gabriel (*Ber.*, 1877, 186) from chloroform and sodium phenyl mercaptide. E. F. A.

Carbithionic Acids. III. The Dithio-, Propionic, Butyric, *iso*Valeric, and *iso*Hexoic Acids. JOSEF HOUBEN and H. POHL (*Ber.*, 1907, 40, 1725—1730. Compare Abstr., 1903, i, 42; 1906, i, 847; this vol., i, 382).—The action of carbon disulphide on organo-magnesium compounds is a general one, and has been extended to acids of the aliphatic series. The acids, $R\cdot CS_2H$, are reddish-yellow oils of unpleasant odour, the salts of the alkalis and alkaline earths are soluble in water, the salts of the heavy metals are, as a rule, unstable.

Ethylcarbithionic [*dithiopropionic*] *acid*, $Et{\cdot}CS_2H$, has b. p. 48°/17 mm., D^{20} 1·12; its *lead* salt is stable. When oxidised by iodine, *thiopropionyl disulphide*, $CSEt{\cdot}S{\cdot}S{\cdot}CSEt$, is obtained. *Propylcarbithionic* [n-*dithiobutyric*] *acid*, $CH_2Et{\cdot}CS_2H$, has b. p. 59°/13 mm., D^{19} 1·08; iso*butylcarbithionic* [*dithio*iso*valeric*] *acid*, $CHMe_2{\cdot}CH_2{\cdot}CS_2H$, b. p. 84°/33 mm., D^{19} 1·008, and iso*amylcarbithionic* [*dithio*iso*hexoic*] *acid*, $CHMe_2{\cdot}[CH_2]_2{\cdot}CS_2H$, b. p. 84°/10 mm., D^{22} 0·98.

The yields of acid obtained vary from 12% to 4·4% of the theoretical.

W. R.

Mercaptal Acids. BROR HOLMBERG and KARL MATTISSON (*Annalen*, 1907, **353**, 123—130. Compare Holmberg, Abstr., 1905, i, 323; Bongartz, Abstr., 1888, 478; Jonsson, *Svensk kemisk tidskrift*, 1904, 22).—Mercaptal acids are formed by the condensation of aldehydes with thiol acids. The authors have prepared such substances by condensation of formaldehyde and benzaldehyde with thiolacetic and thiolpropionic acids.

Methylenedi-thiolacetic acid, $CH_2(S{\cdot}CH_2{\cdot}CO_2H)_2$, is prepared with development of heat by the action of formaldehyde on thiolacetic acid; the velocity of the reaction is increased by addition of hydrochloric or sulphuric acid. It crystallises in white, prismatic leaflets, m. p. 128·5—129°, has the affinity constant $K = 0{\cdot}0461 - 0{\cdot}0586$ with $v = 16 - 512$, is hydrolysed only slowly by hot concentrated hydrochloric acid, and on oxidation with potassium permanganate yields methylenedimethyldisulphone, $CH_2(SO_2Me)_2$. The *sodium*, *sodium hydrogen* (H_2O), and *calcium* (H_2O) salts are analysed; the *ethyl* ester is a colourless oil.

Benzylidenedi-thiolacetic acid, m. p. 126—127° (123—124°: Bongartz, *loc. cit.*), is sparingly soluble in water, and has the affinity constant $K = 0{\cdot}0575 - 0{\cdot}0697$ with $v = 128$—512. The sodium, sodium hydrogen, and barium ($1\frac{1}{2}H_2O$) salts were analysed; the *ethyl* ester is an oil.

Methylenedi-a-thiolpropionic acid, $CH_2(S{\cdot}CHMe{\cdot}CO_2H)_2$, m. p. 130—131°, is prepared by the action of α-thiolpropionic acid on 40% formaldehyde in presence of sulphuric acid.

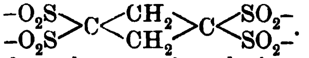
Benzylidenedi-a-thiolpropionic acid, $CHPh(S{\cdot}CHMe{\cdot}CO_2H)_2$, is obtained as a white, crystalline mass, m. p. 138—140°. G. Y.

Methenyltri-thiolacetic Acid. BROR HOLMBERG (*Annalen*, 1907, **353**, 131—138. Compare preceding abstract).—Formic acid reacts with thiolacetic acid in presence of anhydrous zinc chloride, hydrogen chloride, or sulphuric concentrated acid with development of heat, forming *methenyltri-thiolacetic acid*, which is formed also by the action of thiolacetic acid on ethyl formate or formamide saturated with hydrogen chloride.

Methenyltri-thiolacetic acid, $CH(S{\cdot}CH_2{\cdot}CO_2H)_3$, crystallises from water in thin, white leaflets, m. p. 173° evolving gas, has the molecular conductivity $\mu = 58{\cdot}50$ and 210·6, and the affinity coefficient $K = 0{\cdot}090$ and 0·140 with $v = 32$ and 512, and is stable towards dilute acids, but is hydrolysed slowly when boiled with alkali hydroxides or concentrated hydrochloric acid. The *sodium*, *calcium* ($6H_2O$), and *lead* salts are described; the *ethyl* ester forms a colourless oil. The acid is oxidised by bromine in aqueous solution cooled by ice, forming sulphoacetic acid (Stillich, Abstr., 1906, i, 552). G. Y.

Cystine Occurring in Urinary Calculi. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1907, 51, 391—393).—The data adduced show that the cystine obtained from urinary calculi is in the highest probability identical with that obtained from proteins. W. D. H.

Action of Trimethylenetrisulphone on Formaldehyde. ALBERT REYCHLER (*Bull. Soc. chim.*, 1907, [iv], 1, 417—422).—When trimethylenetrisulphone (Baumann and Camps, Abstr., 1890, i, 478; 1892, i, 591) is dissolved in a known quantity of *N*-sodium hydroxide solution and this mixture is titrated with *N*-acid in presence of phenolphthalein, the trimethylenetrisulphone exerts no influence on the reaction, although it is precipitated to some extent towards the end. When formaldehyde is added to such a solution, gelatinisation occurs, unless the solution is dilute, and the author has investigated this action by adding known quantities of the aldehyde to such solutions and determining after an interval of three hours (1) the alkalinity of the system, and (2) the amount of free formaldehyde, by Seyewetz and Gibello's method (Abstr., 1904, ii, 521). The results show that the quantity of formaldehyde absorbed by a molecule of the trisulphone does not increase in proportion with the quantity of aldehyde employed. The principal reaction may be represented by the following equation: $C_3H_6O_6S_3 + 2CH_2O = (C_3H_2O_6S_3)H_2(CH_2{\cdot}OH)_2$, but the compounds $(C_3H_4O_6S_3)H(CH_2{\cdot}OH)$ and $(C_3O_6S_3)H_3(CH_2{\cdot}OH)_3$ are probably also formed in addition to multimolecular compounds having a nucleus such as



$$\begin{matrix}-O_2S\\-O_2S\end{matrix}{>}C{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C{<}\begin{matrix}SO_2-\\SO_2-\end{matrix}.$$

The addition of electrolytes to the solutions causes gelatinisation or the formation of gelatinous precipitates, and opalescence is produced by the addition of much alcohol, but the solutions are not affected by boiling. T. A. H.

Preparation of Acyclic Aldehydes. II. P. BAGARD (*Bull. Soc. chim.*, 1907, [iv], 1, 346—365. Compare this vol., i, 384).—Decoic acid was prepared by reducing ethyl nonoate by Bouveault and Blaise's method (Abstr., 1903, i, 597, 673) and converting the alcohol obtained into the acid through the bromide and cyanide.

a-Bromodecoic acid, m. p. 4°, prepared by treating decoic acid with phosphorus trichloride and bromine, is a colourless liquid at atmospheric temperature, and separates from ether in crystals at − 80°. The *ethyl ester*, b. p. 163—164°/21 mm., is a colourless liquid. The bromo-acid, on treatment with a solution of sodium hydroxide, furnishes *a-hydroxydecoic acid*, m. p. 70·5°, which crystallises from chloroform or light petroleum. The *methyl ester*, m. p. 30°, separates in lamellæ from light petroleum on cooling. The *anilide*, m. p. 79°, crystallises from a mixture of benzene and light petroleum, and the p-*toluidide*, m. p. 100°, crystallises from ethyl acetate. α-*Acetoxydecoic acid*, m. p. 40°, crystallises with difficulty by cooling its solution in light petroleum with methyl chloride. When α-hydroxydecoic acid is heated under the conditions already described (*loc. cit.*) it gives a yield of about 71% of nonaldehyde (Schimmel & Co., Abstr., 1902, i, 345), in addition to small quantities of a polymeride of the aldehyde, an αβ-olefinic acid, and carbon monoxide. No ethylenic hydrocarbon or carbon dioxide is formed in this decomposition (compare this vol., i, 385).

Nonaldehyde semicarbazone, m. p. 100°, separates in small crystals from a mixture of benzene and light petroleum. The *oxime*, m. p. 64°, crystallises from light petroleum and the *azine* is liquid at atmospheric temperature, but crystallises from light petroleum when cooled in methyl chloride. The corresponding naphthacinchoninic acid has m. p. 238—240° (Schimmel & Co., *loc. cit.*). The *diethylacetal*, b. p. 130°/20 mm., is a colourless liquid.

Undecoic acid was prepared by treating undecenoic acid with hydriodic acid and reducing the iodoundecoic acid so formed with zinc turnings in presence of hydrochloric acid. The *anilide*, m. p. 68°, crystallises from a mixture of light petroleum and ethyl acetate and the p-*toluidide*, m. p. 75°, is purified in the same manner as the anilide.

α-*Hydroxyundecoic acid*, m. p. 69°, was prepared by hydrolysing with an aqueous solution of potassium hydroxide the α-bromo-acid obtained by treating undecoic acid with phosphorus trichloride and bromine. It separates in small, brilliant needles from a mixture of light petroleum and chloroform. The *ethyl ester*, m. p. 33°, crystallises from chloroform; the *anilide*, m. p. 80°, crystallises from a mixture of light petroleum and ethyl acetate, and the p-*toluidide*, m. p. 92°, crystallises from ethyl acetate.

When heated, α-hydroxyundecoic acid furnishes about 52% of decaldehyde, small quantities of Δ^{α}-decylene (Grosjean, Abstr., 1892, i, 691), and of a polymeride of the aldehyde and a mixture of carbon monoxide and dioxide. *Decaldoxime*, m. p. 69°, separates in large lamellæ from a mixture of alcohol and water; the *azine*, m. p. 34°, crystallises from benzene, and the corresponding *diethylacetal* has b. p. 133·5°/14 mm.

β-*Ethylnonoic acid*, b. p. 170°/28 mm., was prepared by condensing γ-iodononane with ethyl malonate, hydrolysing the ester of the dibasic acid formed, and distilling the latter. On treatment with phosphorus trichloride and bromine and hydrolysis of the bromo-acid so formed, it furnishes α-*hydroxy*-β-*ethylnonoic acid*, m. p. 47°, which crystallises from light petroleum, on cooling the solution in methyl chloride, and yields an *ethyl ester*, b. p. 148—150°/15 mm. When distilled, the hydroxy-acid gives in addition to α-ethyloctaldehyde, considerable quantities of an ethylenic hydrocarbon, which may have the constitution $C_6H_{13}\cdot CEt\colon CH_2$, and leaves a yellow residue, which is probably an αβ-olefinic acid.

α-*Ethyloctaldehyde*, b. p. 92°/16 mm., is colourless, mobile, and possesses a penetrating odour. The *semicarbazone*, m. p. 53°, is a crystalline powder; the *oxime*, b. p. 131—132°/13 mm., is a colourless liquid, and the corresponding naphthacinchoninic acid, m. p. 190—195°, crystallises from formic acid on the addition of methyl alcohol.

T. A. H.

Preparation of Stable Compounds from Aldehydes and Hyposulphites. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 180529).—By the interaction of 2 mols. of a saturated aldehyde and 1 mol. of a hyposulphite in neutral or acid solution, aldehyde-hyposulphites, $2RCHO,X_2S_2O_4$, are obtained, which are very stable substances, exhibiting the characteristic property of reducing indigotin only on warming. It has now been found that when molecular proportions of an aldehyde and a hyposulphite are mixed in the presence of a compound which will convert an acid sulphite into a normal sulphite, then one half of the sulphur present is eliminated as sulphite, whilst the other half is present in an aldehydesulphoxylate of the type $RCH_2\cdot SO_3X$, R being an organic group and X a univalent metal. The aldehydesulphoxylate is distinguished from the aldehydehyposulphite by the fact that the latter gives a white precipitate with calcium chloride, whilst the former does not.

Sodium formaldehydesulphoxylate, $CH_3\cdot SO_3Na$, is obtained by mixing together in concentrated aqueous solutions molecular proportions of sodium hyposulphite, sodium hydroxide, and formaldehyde; the sodium sulphite produced is precipitated either by concentrating the solution or by adding an equal volume of alcohol, the filtrate on further concentration to a syrupy consistence yields the sulphoxylate. This substance may also be produced by the interaction of zinc hyposulphite, sodium hydroxide, and formaldehyde; the greater portion of the zinc is precipitated as sulphite and the sodium formaldehydesulphoxylate is obtained from the filtrate.

Sodium acetaldehydesulphoxylate resembles the preceding compound, but crystallises even with greater difficulty.

Sodium benzaldehydesulphoxylate is prepared from sodium hyposulphite, sodium hydroxide, and benzaldehyde; the reaction takes place with generation of heat and the new salt separates in long, rectangular prisms.

G. T. M.

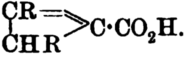
Conversion of Aldehydes into Ketones by Means of Diazomethane. FRITZ SCHLOTTERBECK (*Ber.*, 1907, 40, 1826—1827).—Polemical. A reply to Meyer (this vol., i, 323).

G. Y.

Keten. NORMAN T. M. WILSMORE and ALFRED W. STEWART (*Nature*, 1907, 75, 510).—In contact with a strongly heated platinum wire, acetic anhydride yields a pungent-smelling gas, b. p. about −65°, which solidifies at about −130°, and is obtained also from acetone or in traces by the action of phosphoric oxide or concentrated sulphuric acid on acetic anhydride. The substance, which condenses at the ordinary temperature, forming a pungent, brownish-yellow oil, is absorbed by water and all ordinary reagents, yields an additive compound with bromine and crystalline *compounds* with hydrogen sulphites, is charred by phosphoric oxide or concentrated sulphuric acid, and is considered to have probably the constitution $CH_2\!:\!CO$, and to be the parent substance of the ketens (Staudinger, Abstr., 1905, i, 444). G. Y.

Action of Sodium on Acetone. Raymond Foss Bacon and Paul C. Freer (*Philippine J. Sci.*, 1907, **2**, 67—76. Compare Abstr., 1890, 956; 1891, 1181; 1894, i, 65; Beckmann and Schliebs, Abstr., 1896, i, 124).—As the result of M. Taylor's statement (Trans., 1906, **89**, 1258) that acetone sodium consists chiefly of sodium hydroxide mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone, numerous experiments on the action of sodium on pure acetone in the presence of dry ethyl ether or light petroleum have been repeated and the formation of a sodium derivative of acetone is confirmed. The percentage of sodium is too high, owing to the presence of other sodium compounds, but at least 50% of the original acetone can be recovered from the sodium derivative. It is essential that the materials should be dry and that air should be excluded. J. J. S.

Condensation of Sodium Derivatives of the Acyloins [Hydroxyketones] with Esters of the Acetic Series. Louis Bouveault and René Locquin (*Compt. rend.*, 1907, **144**, 851—853. Compare Abstr., 1906, i, 782).—Since the sodium derivative, $ONa{\cdot}CMe\!:\!CMe{\cdot}ONa$, which gives rise to acetoin on treatment with water, is produced by treating ethyl acetate dissolved in ether with sodium in the cold, it seemed likely that this substance occurs as an intermediate product in the formation of ethyl acetoacetate and that consequently the higher homologues of this ester might be obtained by a direct condensation, which may be represented by the following equation: $ONa{\cdot}CR\!:\!CR{\cdot}ONa + 2EtO{\cdot}Ac = 2R{\cdot}C(ONa)\!:\!CH{\cdot}CO_2Et + 2H_2$. It is found, however, that when the sodium derivatives of the acyloins are condensed with either ethyl or amyl acetate, by heating a mixture of the two substances during four or five hours at 100°, a series of acids is formed, provisionally represented by the following typical formula,



$$\left.\begin{array}{l}CR=\\ |\\ CHR\end{array}\right>C{\cdot}CO_2H.$$

The *acid*, $C_{10}H_{16}O_2$, m. p. 104—105°, b. p. 200—210°/10 mm., formed by condensing the sodium derivative of acetoin with ethyl acetate, crystallises from petroleum, combines with bromine in the cold, evolving hydrogen bromide, and changes when kept to a yellow liquid. Its *methyl* ester, b. p. 142—143°/8 mm., on treatment with ammonia furnishes an *amide*, m. p. 83°, and on reduction with sodium in alcohol yields a saturated *alcohol*, $C_{10}H_{20}O$, b. p. 97—99°/10 mm., which possesses a pleasant odour of mint and furnishes an *acetate*, b. p. 114—115°/16 mm., and a *pyruvate* the *semicarbazone* of which, m. p. 97—98°, crystallises from light petroleum.

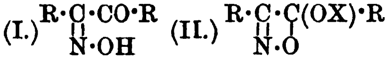
The *acid*, $C_8H_{12}O_2$, b. p. 190—195°/12 mm., obtained by the action of ethyl acetate on the sodium derivative of propionin is a paste. Its *methyl* ester, b. p. 145—150°/20 mm., yields on reduction the *alcohol*, $C_8H_{16}O$, b. p. 90°/15 mm., which furnishes a *pyruvate semicarbazone*, m. p. 114°.

The *product*, $C_{12}H_{20}O_2$, b. p. 205—215°/12 mm., m. p. 151—152°, derived from the sodium derivative of *iso*valeroin gives a *methyl* ester, b. p. 155—160°/12 mm.

The *substance*, $C_{14}H_{24}O_2$, b. p. 230—235°/12 mm., derived from the sodium derivative of hexonoin furnishes a *methyl* ester, b. p. 195—200°/20 mm.

T. A. H.

Diacetylmonoxime. Decomposition of its Benzoyl Derivative. Theory of the Beckmann Transformation. OTTO DIELS and MAX STERN (*Ber.*, 1907, 40, 1629—1633).—Diacetylmonoxime, $\mathrm{COMe\cdot CMe\colon N\cdot OH}$, is a typical *iso*nitrosoketone, colourless in the free state, and forming intensely yellow alkali salts. According to Hantzsch, such compounds are weak acids, and the degree of hydrolysis of their alkali salts is much less than corresponds with the acidity of the substances themselves; *iso*nitrosoketones are *pseudo*-acids of the type (I), whilst the salts are represented by the type (II). This conception is in accordance with the observation that alkaline solutions of *iso*nitrosoketones do not unite with aldehydes, whereas the corresponding oximino-ethers do (compare preceding abstract).



(I.) $\begin{array}{l}\mathrm{R\cdot C\cdot CO\cdot R}\\ \quad\| \\ \quad\mathrm{N\cdot OH}\end{array}$ (II.) $\begin{array}{l}\mathrm{R\cdot C\cdot C(OX)\cdot R}\\ \quad\|\quad | \\ \quad\mathrm{N\cdot O}\end{array}$

The attempt was made by the authors to form condensation products from the benzoyl derivative of diacetylmonoxime,

$$\mathrm{COMe\cdot CMe\colon N\cdot OBz};$$

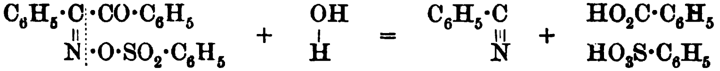
these experiments failed on account of the instability of the benzoate in question towards cold dilute alkalis, which form acetonitrile, benzoic acid, acetic acid, and the dibenzoyl derivative of dimethylglyoxime.

The formation of the latter compound is represented by the scheme:

$$\mathrm{2COMe\cdot CMe\colon N\cdot OBz(+H_2O-H_2O)=}$$
$$\mathrm{COMe\cdot COMe+OBz\cdot N\colon CMe\cdot CMe\colon N\cdot OBz},$$

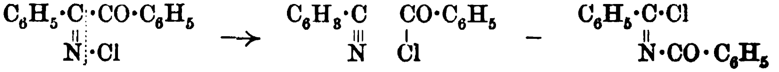
whilst the decomposition into acetonitrile, acetic acid, and benzoic acid is represented by $\mathrm{CH_3\cdot CO\cdot CMe\colon N\cdot O\cdot COPh+H_2O=CH_3\cdot CO_2H+CNMe+Ph\cdot CO_2H}$.

According to Werner and Piguet (Abstr., 1905, i, 66), α-benzilmonoxime, when treated with benzenesulphonyl chloride in alkaline or in pyridine solution, forms benzonitrile and benzoic acid. In this change, it is probable that a benzenesulphonic ester is first formed and then is decomposed by alkali, thus:



$$\begin{array}{l}\mathrm{C_6H_5\cdot C\,\vdots\cdot CO\cdot C_6H_5}\\ \quad\ \| \\ \quad\ \mathrm{N\,\vdots\cdot O\cdot SO_2\cdot C_6H_5}\end{array}+\begin{array}{c}\mathrm{OH}\\ | \\ \mathrm{H}\end{array}=\begin{array}{r}\mathrm{C_6H_5\cdot C}\\ \| | \\ \mathrm{N}\end{array}+\begin{array}{l}\mathrm{HO_2C\cdot C_6H_5}\\ \\ \mathrm{HO_3S\cdot C_6H_5}\end{array}$$

In the Beckmann rearrangement, the intermediate formation of oxime esters is assumed, and the typical nitrile formation is probably the primary action. In the transformation of α-benzilmonoxime by phosphorus pentachloride, for example, the following scheme is submitted:



$$\begin{array}{l}\mathrm{C_6H_5\cdot C\,\vdots\cdot CO\cdot C_6H_5}\\ \quad\ \| \\ \quad\ \mathrm{N\,\vdots\cdot Cl}\end{array}\longrightarrow\begin{array}{r}\mathrm{C_6H_5\cdot C}\\ \| | \\ \mathrm{N}\end{array}\ \begin{array}{l}\mathrm{CO\cdot C_6H_5}\\ | \\ \mathrm{Cl}\end{array}-\begin{array}{l}\mathrm{C_6H_5\cdot C\cdot Cl}\\ \quad\| \\ \quad\mathrm{N\cdot CO\cdot C_6H_5}\end{array}$$

Benzoyldiacetylmonoxime, COPh·O·N:CMe·COMe, obtained by the action of benzoyl chloride on a solution of diacetylmonoxime in sodium hydroxide, separates from alcohol in needles, m. p. 115·5°. When boiled with dilute acids, it is converted into diacetyl, benzoic acid, and hydroxylamine.

Dimethylglyoxime dibenzoate, obtained from the preceding compound, separates from chloroform in rhombic plates, m. p. 223°, and is identical with the compound obtained by the benzoylation of dimethylglyoxime. A. McK.

Dextroses and their Phenylhydrazones and Oximes. ROBERT BEHREND (*Annalen*, 1907, **353**, 106—122. Compare Abstr., 1905, i, 173; Behrend and Roth, Abstr., 1904, i, 716).—The birotation of dextrose has been explained by the assumed existence of two stereoisomeric forms, α- and β-dextrose, which readily undergo transformation one into the other and exist together in equilibrium in solutions with constant rotation. The possibility of the existence of an aldehyde form has also been recognised. When such equilibrium solutions are cooled or evaporated, the form crystallising out must be that the solubility limit of which is reached first. It is found now that whilst α-dextrose can exist in contact with boiling ethyl or *iso*butyl alcoholic solutions, or, in the form of its hydrate, in contact with aqueous solutions, β-dextrose, m. p. 148—150°, $[\alpha]_D$ +20·7°, crystallises from a solution of α-dextrose in boiling pyridine, and is identical probably with Tanret's γ-dextrose (Abstr., 1895, i, 490). A mixture of α- and β-dextrose has m. p. 146—148°.

The phenylhydrazones of dextrose have been re-examined. Skraup's phenylhydrazone (Abstr., 1889, 1130) is formed by shaking dextrose with phenylhydrazine in alcoholic or aqueous alcoholic solution; it crystallises in needles, m. p. 106—107°, and in 5% aqueous solution has the initial rotatory power $[\alpha]_D$ −2°, after twenty minutes $[\alpha]_D$ −5°, and finally $[\alpha]_D$ −50°. Fischer's phenylhydrazone (Abstr., 1887, 567), formed in alcoholic acetic acid solution, crystallises in leaflets, m. p. 159—160°, and in 5% aqueous solution has the initial rotatory power $[\alpha]_D$ −70°, and finally $[\alpha]_D$ −50°. The transformation of the phenylhydrazones into each other takes place also in alcoholic solution, and is accelerated by addition of acetic acid. Skraup's hydrazone crystallises from alcoholic acetic acid cooled by ice, whilst Fischer's compound separates from a similar solution at the ordinary temperature.

If the oil obtained on evaporation of the aqueous solution of dextroseoxime is acetylised in pyridine solution immediately, it forms a *deca-acetyl* compound derived from a condensation product of 2 mols. of dextroseoxime, $C_{12}H_{14}O_{11}NAc_{10}$, which is a viscid oil or colourless, vitreous mass, has $[\alpha]_D$ +36·75° in pyridine solution, and on hydrolysis with sulphuric acid yields acetic acid, hydroxylamine, and dextrose. The condensation of the 2 mols. of dextroseoxime is shown to take place during the acetylation.

Wohl's hexa-acetyldextroseoxime (Abstr., 1893, i, 292), m. p. 110—111°, is formed by the action of acetic anhydride on the oxime, m. p. 138°, in pyridine solution cooled by ice. Acetylation in hot pyridine solution leads to the formation of the hexa-acetyl derivative, together with the deca-acetate and penta-acetylgluconitrile, in amounts varying with the conditions.

On hydrolysis with bromine, freshly prepared solutions of the oxime and solutions with constant rotation yield almost identical mixtures of α- and β-dextrose. G. Y.

Action of Ammonia-Zinc Hydroxide on *d*-Galactose and *l*-Arabinose. KATSUJI INOUYE (*Ber.*, 1907, **40**, 1890—1892. Compare Windaus and Knoop, Abstr., 1905, i, 381, 509; Windaus, this vol., i, 90, 288).—This work was undertaken to determine if methylglyoxaline is formed by the action of a solution of zinc hydroxide in ammonia on sugars other than dextrose.

4 (or 5)-Methylglyoxaline, obtained from *d*-galactose or *l*-arabinose, forms a crystalline mass, m. p. 55—56°; the *picrolonate*,

$$C_4H_6N_2,C_{10}H_8O_5N_4,$$

crystallises in yellow needles, m. p. 287—288·5°. The action of benzoyl chloride and aqueous sodium hydroxide on 4-methylglyoxaline leads to the formation of a *substance*, $C_{17}H_{16}O_2N_2$, crystallising in needles, m. p. 142°, which the author refers to as dibenzoyldiaminoethylene [? *dibenzoyldiaminopropylene*, NHBz·CMe⁚CH·NHBz] (compare Bamberger and Berlé, Abstr., 1892, 632). G. Y.

Scyllitol. JOHANNES MÜLLER (*Ber.*, 1907, **40**, 1821—1826).—In continuation of his studies of naturally occurring alicyclic compounds, the author has undertaken the investigation of scyllitol, discovered by Staedeler and Frerichs (*J. pr. Chem.*, 1858, [i], **73**, 48) in various organs of the *Plagiostomi*. No analysis of scyllit has been published previously.

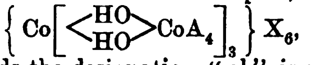
Scyllitol, $C_6H_{12}O_6$, crystallises in hard, glistening, monoclinic prisms, m. p. above 339°, is only sparingly soluble in water, is optically inactive, after careful evaporation with nitric acid gives a red coloration with calcium chloride, and forms a *hexa-acetyl* derivative, $C_6H_6(OAc)_6$. It is concluded that scyllitol is *cyclo*hexan-1:2:3:4:5:6-hexaol and is an *i*-inositol. G. Y.

Inequality of the Resistance of Natural Starch and Artificial Amylose towards Extract of Barley. JULES WOLFF and AUGUSTE FERNBACH (*Compt. rend.*, 1907, **144**, 645—646).—Pure amylose is acted on to a practically equal extent by extract of barley and extract of malt, whilst natural amylose is far more resistant towards barley extract than towards malt extract.

The results show that non-germinated barley contains a diastase which acts on amylose and not on amylopectin. N. H. J. M.

Complex Metal Ammonias. III. Dodecamminehexoltetracobalt and Hexaethylenediaminehexoltetracobalt Salts. ALFRED WERNER [and, in part, E. BERL, GUSTAV JANTSCH, and E. ZINGGELER] (*Ber.*, 1907, **40**, 2103—2125. Compare Abstr., 1898, ii, 223; 1899, ii, 658).—Two series of salts are described having the general formula $\left\{\mathrm{Co}\left[\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}\mathrm{CoA_4}\right]_3\right\}X_6$; in one series, the ammonia series, A represents NH_3, whilst in the other, the ethylenediamine series, A represents $C_2H_4(NH_2)_2$.

These salts represent a second class of basic salts, differing in properties from the hydroxo-compounds described previously. The HO groups have a share in the metallic complex, thus:



$$\left\{\mathrm{Co}\left[<\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}>\mathrm{CoA_4}\right]_3\right\}X_6,$$

and for such compounds the designation "ol" is suggested.

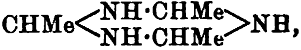
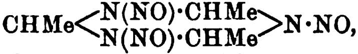
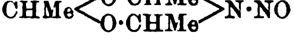
Members of the ammonia series have been obtained by Jörgensen (Abstr., 1898, ii, 226), who termed them anhydrobasic tetramminediaquodiammine salts. They are prepared readily in several ways. *Dodecamminehexoltetracobalt sulphate*, $Co_4H_{42}O_{18}N_{12}S_3,9H_2O$, is obtained by heating dibromotetramminecobalt bromide with a little water until bromine is evolved, and treating the solution of the product with a solution of ammonium sulphate; it is also obtained by adding pyridine to a hot dilute acetic acid solution of diaquotetramminecobalt sulphate. The *dithionate*, $Co_4H_{42}O_{24}N_{12}S_6,4H_2O$, is prepared by adding sodium dithionate and pyridine to a solution of diaquotetramminecobalt chloride in very dilute acetic acid and heating to boiling. The majority of the salts of this series form glistening, brownish-black, well-formed crystals.

The most characteristic salt of the ethylenediamine series is the *nitrate*, $\left[\mathrm{Co}\left(\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}\mathrm{Co\ en_2}\right)_3\right](NO_3)_6,3H_2O$, which is formed when a solution of cobalt nitrate and of ethylenediamine is submitted to atmospheric oxidation; it crystallises in long, dark brown needles, yields *cis*-diaquodiethylenediaminecobalt halide by solution in concentrated hydrochloric or hydrobromic acid, 1 : 6-dichlorodiethylenediaminecobalt chloride by evaporation with dilute hydrochloric acid, and *cis*-hydroxoaquodiethylenediaminecobalt nitrate by treatment with potassium hydroxide. The *bromide*, *iodide*, and *thiocyanate* of the ethylenediamine series are obtained from the nitrate by precipitation, the *chloride* in a similar manner to the nitrate.

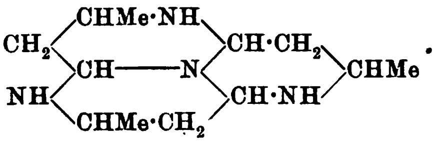
The author rejects Jörgensen's formula for salts of the ammonia series $\left[\begin{matrix}\mathrm{HO}\\ (\mathrm{H_2O})_2\\ (\mathrm{NH_3})_2\end{matrix}\mathrm{Co{\cdot}O{\cdot}}\overset{X}{\mathrm{Co}}(\mathrm{NH_3})_4\right]X_2$, for the following reasons: (1) the salts cannot contain HO directly attached to cobalt, since they do not yield aquo-salts by treatment with mineral acids; (2) in the chloride the presence of chlorine directly attached to cobalt is contrary to the fact that this salt is converted into a halogen-free sulphate by the action of soluble sulphates; (3) the estimation of the products of decomposition of these salts by hydrochloric or hydrobromic acid leads to results contrary to Jörgensen's formula. Thus, the sulphate of the ammonia series yields 81·1% of diaquotetramminecobalt chloride, and the nitrate of the ethylenediamine series, 80·71% of 1 : 6-dichlorodiethylenediaminecobalt nitrate, whereas the amounts calculated from Jörgensen's formula are 68·1% and 54·6% respectively. If the molecular formulæ of these complex salts are doubled and the author's constitutional formula is adopted, the observed percentages in the preceding decompositions agree well with the calculated values; (4) the estimation of the chlorine evolved by the action of cold concentrated hydrochloric acid on salts of either series agrees well with the theory that in the molecule of these salts four cobalt atoms are present, one of which passes from the tervalent to the bivalent state during the decomposition. According to Jörgensen's formula, the products of decomposition must contain one cobalt atom in the form of a tetrammine salt and one cobalt atom as a diammine salt; the latter, in spite of numerous attempts, cannot be detected; (5) the sulphate of the ammonia series is decomposed by dilute sulphuric acid, yielding oxygen, and by concentrated sulphuric acid, evolving oxygen and nitrogen in quantities which agree with those calculated from the author's formula.

The author points out that his formula is the only one which explains satisfactorily the chemical behaviour of these complex salts, particularly with reference to the amount of water, 3 mols., retained by them in the dried state. C. S.

α-Amino- and Imino-acids. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1907, **40**, 1801—1802. Compare this vol., i, 19).—Polemical. A reply to Stadnikoff (this vol., i, 393). J. J. S.

Ethylideneimine (Aldehyde-ammonia) and Hexaethylidenetetramine. MARCEL DELÉPINE (*Compt. rend.*, 1907, **144**, 853—856. Compare Abstr., 1898, i, 462; 1899, i, 326).—Further evidence that aldehyde-ammonia may be regarded as the hydrate of triethylidenetriamine (trimeric ethylideneimine),  $\mathrm{CHMe}<\begin{matrix}\mathrm{NH\cdot CHMe}\\ \mathrm{NH\cdot CHMe}\end{matrix}>\mathrm{NH}$, has been obtained by the preparation of the *trinitroso*-derivative of the latter. This may be obtained by mixing solutions of ethylideneimine and nitrous anhydride in chloroform, or by passing a current of nitrous anhydride into ethylideneimine dissolved in chloroform and cooled by means of methyl chloride. The small yield of the trinitroso-derivative (4—6% of the theoretical) obtained is due to (1) the liberation of water, which transforms part of the imine into the hydrate which is decomposed by nitrous anhydride, and (2) to the production, from impurities contained in the nitrous anhydride, of nitric acid, which reacts with the aldehyde-ammonia, forming ammonium nitrate and aldehyde. The trinitroso-derivative,  $\mathrm{CHMe}<\begin{matrix}\mathrm{N(NO)\cdot CHMe}\\ \mathrm{N(NO)\cdot CHMe}\end{matrix}>\mathrm{N\cdot NO}$, m. p. 161°, crystallises from alcohol in opaque, yellowish-white needles, and from benzene or chloroform in transparent, sulphur-yellow, orthorhombic prisms, which are truncated at the acute angle. It is stable in the dark, but when exposed to light slowly forms traces of brown material insoluble in chloroform. It gives the usual reactions of nitroso-compounds, and is decomposed by warm acetic acid into aldehyde and nitrogen. Hydrochloric acid liberates the nitrogen partly free and partly in the form of nitrous vapours with the formation of some nitrosoparaldimine,  $\mathrm{CHMe}<\begin{matrix}\mathrm{O\cdot CHMe}\\ \mathrm{O\cdot CHMe}\end{matrix}>\mathrm{N\cdot NO}$ (Curtius and Jay, Abstr., 1890, 735).

The hexaethylidenetetramine, described by Kudernatsch (Abstr., 1900, i, 377), is shown to be identical with the tricrotonylidenetetramine, obtained by Wurtz by the action of crotonaldehyde on ammonia at 100° (Abstr., 1879, 780), to which the annexed formula is now assigned.



Crotonaldehyde has D_4^0 0·8715 and D_4^{14} 0·8593 (compare Bauer, *Compt. rend.*, 1860, **51**, 55, and Henninger, Abstr., 1884, 897).

T. A. H.

Occurrence of *l*-Serine in Silk. Emil Fischer (*Ber.*, 1907, **40**, 1501—1505. Compare Abstr., 1906, i, 807).—The presence of derivatives of *l*-serine in the products obtained on hydrolysis of silk has been overlooked in consequence of the much greater solubility in water of the active than of the racemic substances. The residue obtained, on distilling at 140°/0·2—0·5 mm. the esters of the amino-acids formed by hydrolysis of silk or silk fibroin with hydrochloric acid, contains *i*-serine anhydride (Fischer and Suzuki, Abstr., 1906, i, 73) and *l*-serine anhydride. On recrystallisation of the mixture from water, the *l*-anhydride remains in the filtrate and is precipitated on addition of alcohol and cooling with ice as long needles, m. p. 247° (corr.) (decomp.), $[\alpha]_D^{22}$ $-58{\cdot}8°$, which cannot be freed from the racemic compound. When heated with 20% hydrobromic acid at 100°, the *l*-anhydride is converted into l-*seryl*-l-*serine*, $C_6H_{12}O_5N_2$, which crystallises in colourless leaflets, m. p. 234° (corr. decomp.), $[\alpha]_D^{19}$ $+3{\cdot}8°$ in aqueous or $+12°$ in *N*-hydrochloric acid solution, and dissolves with difficulty in boiling water, but does not crystallise out on cooling.

On more prolonged heating with 48% hydrobromic acid at 100°, *l*-serine anhydride yields *l*-serine, which is identical with synthetical *l*-serine in all its properties except the rotatory power, which is smaller, $[\alpha]_D$ $+11{\cdot}6°$ in hydrochloric acid solution, pointing to the presence of 20% of racemic serine in the natural product.

G. Y.

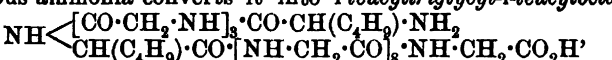
Synthesis of Polypeptides. XVII. Emil Fischer (*Ber.*, 1907, **40**, 1754—1767. Compare Proc., 1907, **23**, 82; this vol., i, 295).—The coupling together of amino-acids has been carried to an octadecapeptide, composed of 15 glycine and 3 *l*-leucine residues. Starting from triglycylglycine and *d*-α-bromo*iso*hexoyldiglycylglycyl chloride, which were condensed in the cold in presence of sodium hydroxide, glass pearls being added to obviate the violent frothing, *d-α-bromo*iso*hexoylhexaglycylglycine* was obtained. This has $[\alpha]_D^{20}$ $+3{\cdot}55°$, becoming 0 after eighteen hours, turns yellow at 246° (corr.) and decomposes above this, and shows a marked biuret coloration. With anhydrous liquid ammonia, it undergoes a Walden rearrangement, forming l-*leucylhexaglycylglycine*,

$$NH_2{\cdot}CH(C_4H_9){\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CO]_6{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

$[\alpha]_D^{20}$ $+6{\cdot}34°$, which turns yellow at 200°, brown at 250°, and decomposes at 300°. The *nitrate*, *sulphate*, and *hydrochloride* form microscopic crystals without definite structure; it shows a marked biuret reaction, and forms a sparingly soluble *copper* salt.

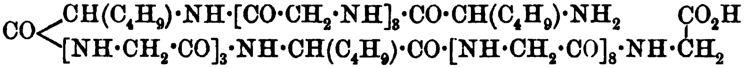
d-*a-Bromo*iso*hexoyloctaglycylglycine* is a colourless, indefinitely crystalline powder, which turns brown at 250° (corr.) and decomposes about 300° (corr.). l-*Leucyloctaglycylglycine*,

$$NH_2·CH(C_4H_9)·CO·[NH·CH_2·CO]_8·NH·CH_2·CO_2H,$$

becomes brown at 260° and black at 300°, and gives a red biuret coloration. It condenses with *d*-*a*-bromo*iso*hexoyldiglycylglycyl chloride to d-*a-bromo*iso*hexoyltriglycyl-leucyloctaglycylglycine*, a colourless solid which turns brown at 255° and decomposes at 305°. Liquid anhydrous ammonia converts it into l-*leucyltriglycyl*-l-*leucyloctaglycylglycine*,  $NH<\begin{array}{l}[CO·CH_2·NH]_3·CO·CH(C_4H_9)·NH_2\\ CH(C_4H_9)·CO·[NH·CH_2·CO]_8·NH·CH_2·CO_2H\end{array}$, which becomes brown at 235° and decomposes without melting; it shows a cherry-red biuret coloration, is precipitated by ammonium sulphate, tannin and phosphotungstic acid, and the *nitrate* forms large, almost crystalline granules.

d-*a-Bromo*iso*hexoyltriglycyl*-l-*leucyltriglycyl*-l-*leucyloctaglycylglycine* is obtained by repeating the condensation of the tetradecapeptide with the bromo-compound as a granular precipitate, which turns brown at 240° and froths and decomposes at 310° (corr.).

l-*Leucyltriglycyl*-l-*leucyltriglycyl*-l-*leucyloctaglycylglycine*,



$$CO<\begin{array}{l}CH(C_4H_9)·NH·[CO·CH_2·NH]_8·CO·CH(C_4H_9)·NH_2 \qquad CO_2H\\ [NH·CH_2·CO]_3·NH·CH(C_4H_9)·CO·[NH·CH_2·CO]_8·NH·\overset{|}{CH_2}\end{array}$$

forms a colourless powder which dissolves in 100 parts of boiling water; the aqueous solution froths considerably, and gives precipitates with ammonium sulphate, phosphotungstic acid, or tannin.

These four polypeptides closely resemble the natural proteins; they do not show the colour reactions of Millon and Adamkiewicz, or the xanthoprotein and sulphur reactions, since they do not contain tyrosine, tryptophan, or cystine. The octadecapeptide has a molecular weight of 1213, and is thus the substance of highest molecular weight of which the constitution is known.

d-*Bromopropionyl*-l-*leucine* crystallises in narrow needles aggregated in bundles, m. p. 50—51° (corr.), $[a]_D^{20}$ $-5·8°$. d-*Alanyl*-l-*leucine* forms narrow-pointed plates from water or lens-like, four-sided plates from alcohol; m. p. 255—256° (corr.), $[a]_D^{20}$ $-17°$. E. F. A.

Synthesis of Polypeptides. XVIII. Derivatives of Aspartic Acid. Emil Fischer and Ernst Koenigs (*Ber.*, 1907, 40, 2048—2061. Compare Abstr., 1905, i, 31).—The two isomeric leucylasparagines, previously obtained as a mixture, have been prepared in larger quantity and separated. By hydrolysis of one of them with acid and examination of the leucine obtained, the constitution of the dipeptides and the corresponding *a*-bromo*iso*hexoylasparagines is established.

The separation of the active bromo-derivatives was effected by means of the fractional precipitation of the alkaline solution with normal hydrochloric acid, the *l*-*a*-bromo*iso*hexoic acid derivative being sparingly soluble. *l*-*a*-Bromo*iso*hexoyl-*l*-asparagine has $[a]_D^{20}$ $-30·1°$, and is soluble in 200—300 parts of water; *d*-*a*-bromo*iso*hexoyl *l*-asparagine crystallises with $1H_2O$ in stellar aggregates of long, narrow prisms, m. p. 146—148°, has $[\alpha]_D^{20}$ $+15\cdot7^{\circ}$, and is soluble in 100—150 parts water at 25°.

d-*Leucyl*-l-*asparagine* crystallises in colourless prisms and domes, m. p. 230° (corr. decomp.), and has $[\alpha]_D^{20}$ $-53\cdot6^{\circ}$; l-*leucyl*-l-*asparagine* forms needles or prisms, m. p. 228° (corr.), has $[\alpha]_D^{20}$ $+17\cdot8^{\circ}$, and gives a bluish-violet coloration with alkali and a copper salt; it yields *l*-leucine when hydrolysed.

α-Bromo*iso*hexoyl-*l*-asparagine, when shaken with acetyl chloride, yields a compound, $C_{10}H_{16}O_4N_2$, m. p. 128—130° (corr.), which is optically inactive, soluble in alkali, and yields ammonia on boiling. It gives complicated decomposition products with sulphuric acid, and is of, as yet, unknown constitution.

Chloroacetyl-l-*asparaginyl chloride*,

$$CH_2Cl\cdot CO\cdot NH\cdot CH\cdot(CH_2\cdot CO\cdot NH_2)\cdot COCl,$$

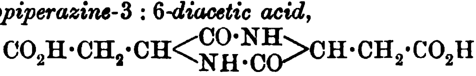
prepared by the action of acetyl chloride on chloroacetyl-*l*-asparagine, can be coupled with l-*leucine ester* to *ethyl chloroacetyl*-l-*asparaginyl*-l-*leucine* crystallising in microscopic needles, m. p. 166—167° (corr.); it tastes bitter. *Chloroacetyl*-l-*asparaginyl*-l-*leucine* forms bunches of centimetre long, pointed prisms, m. p. 167° (corr., red coloration), and does not taste bitter. The tripeptide, *glycyl*-l-*asparaginyl*-l-*leucine*,

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH(CH_2\cdot CO\cdot NH_2)\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO_2H,$$

obtained by the action of liquid ammonia on the foregoing, crystallises in nodular aggregates of microscopic needles and has $[\alpha]_D^{20}$ $-46\cdot5^{\circ}$.

Methyl l-*aspartate* is a colourless liquid, b. p. 119—120°/15 mm., which on heating for three days at 100° forms *methyl* 2 : 5-*diketopiperazine*-3 : 6-*diacetate*, crystallising in bunches of microscopic needles or long, thin prisms.

2 : 5-*Diketopiperazine*-3 : 6-*diacetic acid*,



$$CO_2H\cdot CH_2\cdot CH\begin{matrix}<CO\cdot NH>\\ <NH\cdot CO>\end{matrix}CH\cdot CH_2\cdot CO_2H,$$

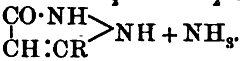
forms small, oblique plates or prisms decomposing at 300°. When left in the cold with barium hydroxide, it forms a compound, $C_8H_{12}O_7N_2$, probably *asparagylaspartic acid*,

$$CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H;$$

this decomposes at 120°. E. F. A.

Method of Synthesis of β-Ketonic Non-substituted Amides.

Charles Moureu and I. Lazennec (*Compt. rend.*, 1907, **144**, 806—808. Compare *Bull. Soc. chim.*, 1906 [iii], **35**, 523).—By heating the alcoholic solution of an acetylenic amide with a small quantity of a secondary amine (preferably piperidine) for some hours, under a reflux condenser, the corresponding β-ketonic amide is formed. With aliphatic amides only a few drops of piperidine are necessary, but with phenylpropiolamide an equal molecular quantity is required. The piperidine appears to act catalytically by the formation of an intermediate compound, and a compound, $C_5NH_{10}\cdot CPh\colon CH\cdot CO\cdot NH_2$, m. p. 135—136°, has actually been isolated from phenylpropiolamide, and when treated with oxalic acid in ether-alcoholic solution gives piperidine oxalate and benzoylacetamide. The β-ketonic amides are soluble in aqueous alkali hydroxide solutions, and their alcoholic solutions give an intense reddish-violet coloration with ferric chloride. The constitution is confirmed by condensation with hydrazine hydrate to the corresponding pyrazolones with elimination of ammonia: $R\cdot CO\cdot CH_2\cdot CO\cdot NH_2 + N_2H_4 \longrightarrow R\cdot C({:}CH\cdot CO\cdot NH_2)\cdot NH\cdot NH_2 \longrightarrow$



$$\begin{array}{l}CO\cdot NH\\ \vert\\ CH{:}CR\end{array}\!\!>NH + NH_3.$$

Hexoylacetamide, $C_5H_{11}\cdot CO\cdot CH_2\cdot CO\cdot NH_2$, has m. p. 99—100°; *heptoylacetamide*, $C_6H_{13}\cdot CO\cdot CH_2\cdot CO\cdot NH_2$, has m. p. 106—107°. Benzoylacetamide, previously obtained by Obrégia (Abstr., 1892, 324) and Guareschi (Abstr., 1904, i, 891), was also prepared.

E. H.

Direct Hydrogenation of Carbimides.

PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, **144**, 824—826).—When a current of hydrogen impregnated with the vapour of ethylcarbimide is passed over nickel heated at 180—190° the issuing gas contains ammonia and carbon dioxide, but is free from methane and carbon monoxide, and when passed into a cooled receptacle deposits a liquid containing small quantities of mono-, di-, and tri-ethylamine, but chiefly constituted by methylethylamine. The principal reaction may be represented by the equation: $Et\cdot N{:}CO + 3H_2 = H_2O + NHMeEt$. The secondary products are due to the formation of some diethylcarbamide by the action of the water produced on a portion of the ethylcarbimide, with the subsequent reduction of the diethylcarbamide to methylethylamine and ethylamine, the latter then giving rise in contact with the nickel to some di- and tri-ethylamine (compare Sabatier and Senderens, Abstr., 1905, i, 267; Mailhe, Abstr., 1905, i, 571, 635). When phenylcarbimide is reduced under similar conditions, the issuing gas contains methane and carbon dioxide; the tube containing the nickel becomes coated with crystals of diphenylcarbamide, and the liquid product obtained when the gas is cooled consists of water and aniline. The principal reaction may be represented by the equation: $Ph\cdot N{:}CO + 4H_2 = NH_2Ph + CH_4 + H_2O$. Most of the water formed reacts with some of the phenylcarbimide to produce diphenylcarbamide. The tendency of phenylcarbimide to produce aniline on reduction has already been observed by Gumpert (Abstr., 1885, 656).

T. A. H.

Trichloroacetimido-methyl Ether.

WILHELM STEINKOPF (*Ber.*, 1907, **40**, 1643—1646).—*Trichloroacetimido-methyl ether*,

$$CCl_3\cdot C({:}NH)\cdot OMe,$$

b. p. 148—149°, is a colourless oil of terpene-like odour, obtained by heating trichloroacetonitrile and methyl alcohol on the water-bath. Hydrogen chloride decomposes it in ethereal or alcoholic solution with the separation of ammonium chloride. Attempts to prepare the hydrochloride by Pinner's method lead to the formation of trichloroacetamide. When the methyl ether is heated with aniline, *trichloroacetophenylamidine*, $CCl_3\cdot C(NH)\cdot NHPh$, m. p. 101°, is obtained, which is not changed by water at 100°, and evolves the odour of phenylcarbylamine when treated with warm dilute sodium hydroxide; the *hydrochloride*, $C_8H_7N_2Cl_3,HCl$, sinters and darkens at 171° and has m. p. 183°; the *platinichloride*, $C_{16}H_{14}N_4Cl_6,H_2PtCl_6,H_2O$, is mentioned.

C. S.

Remarkable Additive Reaction of Fulminic Acid. F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 545—552).—The author discusses Nef's carbyloxime formula, $C\vdots N\cdot OH$, for fulminic acid and shows that Jovitschitsch's objections to it (Abstr., 1906, i, 732) are invalid. His own investigations are then described.

Fulminic acid yields a hydrobromide resembling the hydrochloride in being extremely volatile and disagreeable to work with. The *hydriodide*, m. p. 65°, however, is more stable, and, with aniline in ethereal solution, gives phenyl*iso*urethane and, with aqueous silver nitrate, quantitative yields of silver iodide and fulminate; its aqueous solution is strongly acid.

One of the products of the action of nitrous acid on fulminic acid is found to be methylnitrolic acid or nitroformoxime,

$$NO_2\cdot CH\vdots N\cdot OH,$$

which supports Nef's carbyloxime structure for fulminic acid.

T. H. P.

Anhydrous Thiocyanic Acid. ARTHUR ROSENHEIM and RICHARD LEVY (*Ber.*, 1907, 40, 2166—2169).—When concentrated sulphuric acid is allowed to drop slowly on to a mixture of dry potassium thiocyanate and phosphoric oxide in an atmosphere of hydrogen at 40—60 mm. pressure, pure thiocyanic acid, m. p. about 5°, is obtained and condenses in a cooled receiver in the form of white crystals. It has a corrosive action on the skin, is soluble in water at 0° without decomposition, but at higher temperatures changes rapidly to a yellow polymeride.

C. S.

Comparisons of Nitriles and *iso*Nitriles in their Behaviour towards Metallic Salts. Constitution of Double Cyanides. KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1907, 40, 1772—1778).—The behaviour of nitriles and carbylamines towards certain metallic salts has been examined in order to determine which of these two groups of compounds resembles potassium cyanide in its power of forming complex cyanides. No stable compounds of nitriles or carbylamines with silver cyanide have been isolated. The compound AgCN,EtNC (E. Meyer, *J. pr. Chem.*, 1856, [i], 67, 147; A. W. Hoffmann, *Annalen*, 1867, 144, 118) is extremely unstable.

Platinous chloride readily forms the additive compound, *platinous chloride bisphenylcarbylamine*, $PtCl_2,2PhNC$, which crystallises in purple-coloured prisms almost insoluble in ether and other organic solvents. It is extremely stable towards water and dilute alkalis, and potassium sulphide acts but slowly on a hot solution. The chlorine is also difficult to remove from the molecule.

An isomeric compound, *platinous chloride bisbenzonitrile*, is slowly deposited when an ethereal solution of the nitrile is mixed with an aqueous solution of potassium platinochloride. It forms pale yellow crystals showing double refraction, dissolves in hot sodium hydroxide solution or in warm potassium cyanide solution, liberating the nitrile. It does not react with silver nitrate. A similar compound of acetonitrile and platinous chloride has been obtained.

Phenylcarbylamine forms the unstable compound 2AgCN,PhNC, which gradually gives up the carbylamine. Cuprous cyanide forms an unstable compound, CuCN,2EtNC. Benzonitrile combines with neither silver nor mercurous cyanide.

J. J. S.

Direct Hydrogenation of Aliphatic *iso*Cyanides [Carbylamines].

Paul Sabatier and **Alphonse Mailhe** (*Compt. rend.*, 1907, **144**, 955—957. Compare Abstr., 1905, i, 267, this vol., i, 458, 488).—When a current of hydrogen, impregnated with an aliphatic carbylamine, is passed over a column of reduced nickel, heated at 160—180°, the carbylamine is reduced, for the most part, to the corresponding *sec.*-amine, but a portion is converted into the isomeric cyanide, which in turn is reduced, whilst a third portion is polymerised with the formation of tarry matter, which is deposited on the nickel and impedes its reducing action so that ultimately a portion of the carbylamine escapes unchanged. If the reduction is conducted at 220—250°, the *sec.*-amine formed suffers decomposition with the production of hydrogen, hydrocarbons, and ammonia, especially in the case of the more complex carbylamines.

Methylcarbylamine furnishes principally dimethylamine together with small quantities of ethylamine and diethylamine. Ethylcarbylamine similarly yields methylethylamine accompanied by smaller quantities of propylamine and dipropylamine. *tert.*-Butylcarbylamine, $CMe_3 \cdot NC$, furnishes on reduction methyl-*tert.*-butylamine accompanied by dimethylpropylamine, b. p. 83°, and a small quantity of an amine of higher b. p. *Methyl-*tert.*-butylamine*, $CMe_3 \cdot NHMe$, b. p. 58—60°, is a colourless, mobile liquid with a penetrating, but not disagreeable, odour. It yields an oily *nitroso*-derivative. The *carbonate* becomes yellow on keeping; the *hydrochloride* is deliquescent; the *oxalate* has m. p. 160° (decomp.). With phenylcarbimide the amine furnishes *β-phenyl-α-methyl α-*tert.*-butylcarbamide*, m. p. 118°, which crystallises from alcohol in needles or rhombic lamellæ.

T. A. H.

Attempts to Synthesise Nitroacetonitrile. II. Halogenated Amino-oximes.

Wilhelm Steinkopf and **Ludwig Bohrmann** (*Ber.*, 1907, **40**, 1633—1643. Compare Abstr., 1905, i, 122).—Unsuccessful attempts have been made to obtain nitroacetonitrile from nitroacetamide and phosphoric oxide, from bromonitromethane and potassium cyanide, and by the nitration of ethyl cyanoacetate. Cyanoformaldehyde also could not be prepared.

A series of α-halogenated amino-oximes has been prepared from α-halogenated acetonitriles and hydroxylamine in neutral, aqueous solution. These compounds differ strikingly from unsubstituted amino-oximes in the rapidity of their formation and in their stability to boiling water, hydroxylamine being eliminated only in sealed tubes at 100°, or by the action of hot alkalis.

α-Chloroethenylamino-oxime, $CH_2Cl \cdot C(NH_2)\colon NOH$, m. p. 91—92°

(decomp.), obtained from chloroacetonitrile, crystallises from benzene in long needles, and reduces a boiling alkaline solution of mercuric chloride; the *hydrochloride*, $C_2H_5ON_2Cl,HCl$, has m. p. 116—118° (decomp.).

aa-Dichloroethenylamino-oxime, $CHCl_2\cdot C(NH_2){:}N\cdot OH$, m. p. 103—104° (decomp.), prepared from dichloroacetonitrile, gives a violet coloration with ferric chloride, yellow precipitates with sodium or ammonium hydroxides, a white silver salt, and a bluish-green copper salt; the *hydrochloride*, $C_2H_4ON_2Cl_2,HCl$, has m. p. 135° (decomp.), and the *acetyl* derivative, $CHCl_2\cdot C(N\cdot OH)\cdot NHAc$, obtained by evaporating a solution in acetic anhydride over potassium hydroxide in a vacuum, has m. p. 114—115°. *Oximinoethenylamino-oxime*, $OH\cdot N{:}CH\cdot C(NH_2){:}N\cdot OH$, m. p. 148—152° (decomp.), is obtained by treating the preceding amino-oxime or dichloroacetonitrile with an excess of neutral hydroxylamine at 60°; it reduces solutions of silver, copper, and mercury salts, and is precipitated from its concentrated aqueous solution by nickel acetate in the form of a reddish-brown *nickel* salt, $C_4H_8O_4N_6Ni$, which dissolves in dilute sulphuric acid to a colourless solution. By evaporating the solution of oximinoethenylamino oxime in acetic anhydride in a vacuum over potassium hydroxide, the *diacetyl* compound, $OAc\cdot N{:}CH\cdot C(N\cdot OH)\cdot NHAc$, m. p. 142—150°, is obtained, which is identical with the product obtained by treating Söderbaum's acetyl*iso*nitrosoacetonitrile (Abstr., 1892, 815) with hydroxylamine and acetylating the resulting amino-oxime.

Trichloroethenylamino-oxime, $CCl_3\cdot C(NH_2){:}N\cdot OH$, m. p. 128—129° (decomp.), crystallises in glistening leaflets; the *hydrochloride* has m. p. 149° (decomp.). By treating trichloroacetonitrile with 2 mols. of hydroxylamine at 65°, *a-chloro-oximinoethenylamino-oxime*,

$$CCl(N\cdot OH)\cdot C(NH_2){:}N\cdot OH,$$

m. p. 109° (decomp.), is obtained, which gives a deep reddish-brown coloration with ferric chloride.

Iodoethenylamino-oxime, $CH_2I\cdot C(NH_2){:}N\cdot OH$, m. p. 123—124° (decomp.), is prepared from iodoacetonitrile and hydroxylamine in methyl-alcoholic solution; the *acetyl* derivative,

$$CH_2I\cdot C(N\cdot OH)\cdot NHAc,$$

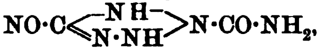
has m. p. 103—105°. C. S.

Cyanogen Bromide and Hydroxylamine. III. Heinrich Wieland and Hugo Bauer (*Ber.*, 1907, 40, 1680—1691. Compare Abstr., 1904, i, 628; 1905, i, 420; this vol., i, 494).—The azoxydicarboxylamidedioxime, produced by the action of alkali on dihydroxyguanidine, results probably from the condensation of unchanged substance with aminomethylnitrosolic acid,

$$OH\cdot N{:}C(NH_2)\cdot NO + OH\cdot N{:}C(NH_2)\cdot NH\cdot OH = OH\cdot N{:}C(NH_2)\cdot ON_2\cdot C(NH_2){:}N\cdot OH + H_2O,$$

the nitrosolic acid being derived from the hydrolysis of the azo-derivative, $OH\cdot N{:}C(NH_2)\cdot N{:}N\cdot C(NH_2){:}N\cdot OH$. In alkaline solution this compound undergoes isomeric change into the hydrazone, *amino-azaurolic acid*, $ON\cdot C(NH_2){:}N\cdot NH\cdot C(NH_2){:}N\cdot OH$, which crystallises from hot water in long, orange-red needles with a blue reflex, exploding at 184°. In preparing this substance, the temperature and concentration exert a great influence. The *silver* salt is brick-red, the *copper* salt is dark reddish-brown. On reduction with hydrogen sulphide, *hydrazodicarboxylamideoxime*, $NH_2\cdot CO\cdot NH\cdot NH\cdot C(NH_2):NOH$, is obtained quantitatively in colourless needles from water, decomposing at 220°; the *silver* salt is colourless. As distinguished from hydrazodicarboxylamide (Thiele, Abstr., 1892, 1298, 1429), this hydrazo-derivative is easily oxidised by chromic acid or nitric acid to an unstable azo-compound. It is, however, very stable towards acids, no elimination of hydroxylamine occurring.

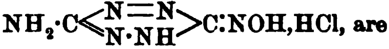
5-*Nitrosodihydrotetrazole-2-carboxylamide*,



$$NO\cdot C{<}\genfrac{}{}{0pt}{}{NH-}{N\cdot NH}{>}N\cdot CO\cdot NH_2,$$

results from the interaction of hydrazodicarboxylamideoxime and nitrous acid, mixed probably with an azo-compound, as a red, explosive substance. The above constitution is assigned to the substance, as nitrous acid is obtained on hydrolysis by acids.

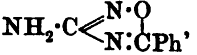
When aminoazaurolic acid is boiled with 18% hydrochloric acid, the solution suddenly changes to a dark green colour and finally becomes honey-yellow, nitrogen and carbon dioxide being evolved at the same time. On cooling, orange-yellow crystals of the *hydrochloride* of iso*nitrosoaminohydrotetrazine*, $NH_2\cdot C{<}\genfrac{}{}{0pt}{}{N=N}{N\cdot NH}{>}C:NOH,HCl$, are obtained, which do not decompose at 350°. In addition to the tetrazine being a mono-acid base, it gives a dark red *silver* salt, $C_2H_8O_6N_6Ag$.



Benzoylation of Dihydroxyguanidine.—Experiments made to methylate or benzoylate azodicarboxylamidedioxime by means of methyl sulphate or benzoyl chloride either in sodium carbonate or sodium hydrogen carbonate solution, were without result. When dihydroxyguanidine and benzoyl chloride interact in the presence of sodium hydrogen carbonate, a chrome-yellow mass first separates and afterwards colourless crystals. The yellow material consists largely of *azoxydicarboxylamidedioxime dibenzoate*, $ON_2[C(NH_2):NOBz]_2$, purified by repeated shaking with acetone until it is completely soluble in dilute sodium hydroxide, which quickly causes decomposition into benzoic acid, nitrogen, and hydroxycarbamide. At 155° it decomposes explosively. The colourless crystalline portion consists of dibenzhydroxamic acid and *benzoylguanidine benzoate*,

$$NHBz\cdot C(NH_2):N\cdot OBz,$$

crystallising from alcohol in needles decomposing at 162—163°. When warmed with alkalis or acids, benzoylguanidine benzoate gives benzoic acid and *aminophenylazoxime*, $NH_2\cdot C{<}\genfrac{}{}{0pt}{}{N\cdot O}{N:CPh}$, crystallising in needles, m. p. 164°. Alkaline permanganate is without action on the substance, which forms a *silver* salt. W. R.



Acethydroxamic Chloride. HEINRICH WIELAND (*Ber.*, 1907, 40, 1676—1680. Compare Piloty and Steinbock, Abstr., 1902, i, 735).—A method for preparing acethydroxamic chloride in nearly quantitative yield directly from acetaldoxime and chlorine is described; its derivatives from amines and phenols are well-defined, crystalline substances, and the chloride is therefore a suitable reagent for characterising these classes of compounds.

The interaction of the chloride and hydrazine results in the formation, not of a hydrazo-compound, but of aminodimethyltriazole; aniline gives acetanilide-oxime (Nordmann, Abstr., 1885, 238), and phenylhydrazine, phenylhydrazoacetaldoxime (Bamberger, Abstr., 1902, i, 247). *Acet-p-phenetide-oxime*, $OEt\cdot C_6H_4\cdot NH\cdot CMe:NOH$, from the acethydroxamic chloride and the corresponding amine, crystallises in large, colourless plates from alcohol, m. p. 148°, and forms a *hydrochloride*. Ferric chloride gives a very intense, carmine-red coloration. The *acetate*, $C_{12}H_{16}O_3N_2$, crystallises in prisms, m. p. 117—118°. The *oxime* of *o*-acetoxybenzoic acid, $C_9H_9O_4N$, crystallises in plates, m. p. 100°, and gives a red coloration with ferric chloride. W. R.

Isomeric Dioximinosuccinic Acids. André Wahl (*Compt. rend.*, 1907, **144**, 922—924. Compare Abstr., 1906, i, 624).—By application of Söderbaum's method (Abstr., 1891, 825) to sodium dihydroxytartrate, extraction of the product with ether, and evaporation of the ethereal solution, a viscid liquid is obtained which, in a vacuum, is completely converted into a pale yellow, crystalline mass. The latter on repeated fractional crystallisation gives (1) a small quantity of oxalic acid; (2) transparent crystals of *iso*nitrosocyanoacetic acid, and (3) hemispherical aggregates of crystalline prisms, which, after drying in a vacuum, have the composition

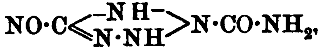
$$C_4H_4O_6N_2,\tfrac{1}{2}C_6H_6.$$

The benzene of crystallisation is lost at 190°, leaving a residue having the composition of dioximinosuccinic acid. The latter forms very hard, white crystals, m. p. 168—170° (decomp.), of which the aqueous solution gives white precipitates with silver nitrate and calcium acetate, and with cupric acetate a green precipitate which is transformed into a bluish-green, crystalline substance on heating or keeping. The two isomeric acids described by Söderbaum have m. p. 145—150°, and of these the $\beta\beta$-acid with cupric acetate gives a dirty green precipitate becoming brown.

If a current of dry hydrogen chloride is passed through a solution of ethyl dioximinosuccinate in anhydrous ether and the solution is evaporated in a vacuum over potash, the product is a white, crystalline substance having the same composition as the original ester, but different properties. It crystallises from water in fine, felted needles, m. p. 140°, and can be purified through the *silver* salt. The latter, obtained by adding silver nitrate to an aqueous solution of the acid, forms explosive, white crystals, which blacken in air, have a composition corresponding with the formula $C_8H_{12}O_6N_2,AgNO_3$, and are decomposed by an equivalent amount of sodium chloride, liberating the ester in a pure state. The latter has the same composition and molecular weight as the original ester, but differs from it in melting point (143°), solubility, and reaction with silver nitrate. This isomeric transformation is also effected by acetyl chloride, but not by acetic anhydride, which gives the *diacetate* of the ester in the form of colourless prisms, m. p. 105°. E. H.

tion exert a great influence. The *silver* salt is brick-red, the *copper* salt is dark reddish-brown. On reduction with hydrogen sulphide, *hydrazodicarboxylamideoxime*, $NH_2\cdot CO\cdot NH\cdot NH\cdot C(NH_2)\colon NOH$, is obtained quantitatively in colourless needles from water, decomposing at 220°; the *silver* salt is colourless. As distinguished from hydrazodicarboxylamide (Thiele, Abstr., 1892, 1298, 1429), this hydrazo-derivative is easily oxidised by chromic acid or nitric acid to an unstable azo-compound. It is, however, very stable towards acids, no elimination of hydroxylamine occurring.

5-*Nitrosodihydrotetrazole*-2-*carboxylamide*,

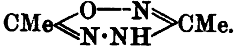


$$\mathrm{NO{\cdot}C}\lessdot\begin{matrix}\mathrm{-NH-}\\ \mathrm{N{\cdot}NH}\end{matrix}\gtrdot\mathrm{N{\cdot}CO{\cdot}NH_2},$$

results from the interaction of hydr[illegible] the azaurolic acid. nitrous acid, mixed prob[illegible] product of ethylnitrolic acid con- explosive substan[illegible]ounts of *acethydroxylamino-oxime*, which under- substa[illegible] conversion into the azaurolic acid only slowly at the low temperature of the reduction. It is shown further that when treated with cooled 40% aqueous alkalis, *acethydroxylamino-oxime*, prepared by the action of hydroxylamine on acethydroxamyl chloride, yields ethylazaurolic acid, which is formed thus in the absence of a reducing agent.

As an aliphatic azo-compound, ethylazaurolic acid was expected to undergo hydrolysis in the same manner as the azo-compound derived from dihydroxyguanidine (Wieland, *loc. cit.*), forming ethylnitrosolic acid and acetamino-oxine, $OH\cdot N\colon CMe\cdot NO + NH_2\cdot CMe\colon N\cdot OH$; this expectation was not realised, the azaurolic acid, as shown by Meyer and Constam, being stable towards alkalis. On the other hand, in agreement with the second or hydrazone constitution, ethylazaurolic acid is decomposed by moderately concentrated acids, evolving nitrous acid, and by boiling water, with loss of $NOH(2NOH = N_2O + H_2O)$, reactions which are characteristic of the grouping $\cdot N\colon CR\cdot NO$, as contained in benzylnitrosolic acid (Wieland and Bauer, *loc. cit.*). The products, nitrous acid, hydrazine, hydroxylamine, nitrogen, and acetic acid, obtained by the action of acids on the azaurolic acid, point to the decomposition taking place partly directly, partly after intermediate change into the isomeric azo-form. Acetaldehyde, which would be expected in both cases, could not be detected. Traces of nitrous oxide and of leucazone are also formed.

Leucazone, which is formed from ethylazaurolic acid by the action of boiling water, or together with ammonia by reduction of the azaurolic acid with hydrogen sulphide, is considered to have the constitution



$$\mathrm{CMe}\lessdot\begin{matrix}\mathrm{O{-}N}\\ \mathrm{N{\cdot}NH}\end{matrix}\gtrdot\mathrm{CMe}.$$

In the stability of its hydrazone form, ethylazaurolic acid is in opposition to Bamberger's nitroso-derivatives of aldehydephenylhydrazones (Abstr., 1903, i, 283), which are stable in the azo-form, $OH\cdot N\colon CR\cdot N\colon NPh$. This difference in the stabilities of such azo- and hydrazone compounds appears to be a characteristic difference of aromatic and aliphatic compounds.

Similarly to dihydroxyguanidine and benzenylhydroxylamino-oxime, acethydroxylamino-oxime can be converted, by the action of stances, and the chloride is therefore a suitable reagent for characterising these classes of compounds.

The interaction of the chloride and hydrazine results in the formation, not of a hydrazo-compound, but of aminodimethyltriazole; aniline gives acetanilide-oxime (Nordmann, Abstr., 1885, 238), and phenylhydrazine, phenylhydrazoacetaldoxime (Bamberger, Abstr., 1902, i, 247). *Acet-p-phenetide-oxime*, $OEt\cdot C_6H_4\cdot NH\cdot CMe:NOH$, from the acethydroxamic chloride and the corresponding amine, crystallises in large, colourless plates from alcohol, m. p. 148°, and forms a *hydrochloride*. Ferric chloride gives a very intense, carmine-red coloration. The *acetate*, $C_{12}H_{16}O_3N_2$, crystallises in prisms, m. p. 117—118°. The *oxime* of [illegible] [illegible] acid, [illegible], crystallises in plates, m. p. 100°, and $ON_2(CMe:N\cdot OH)_2$, is unstable, [illegible]. W. R.
acethydroxamic acid and nitrogen, and, on [illegible]
and nitrosoacethydroxylamino-oxime, but in concen[illegible]
solution undergoes transformation into the stable *ethylhydroxyazaurolic acid*, $NO\cdot CMe:N\cdot N(OH)\cdot CMe:N\cdot OH$, which on reduction yields ethylazaurolic acid, and is decomposed by boiling water, forming *hydroxyleucazone*.

Dibenzoylethylazaurolic acid, $NO\cdot CMe:N\cdot NBz\cdot CMe:N\cdot OBz$, crystallises in orange-red needles, m. p. 210° (decomp.).

Acethydroxylamino-oxime hydrochloride, $C_2H_6O_2N_2,HCl$, forms long, colourless needles, m. p. 156° (decomp.), gives a blue coloration with ferric chloride, reduces ammoniacal silver nitrate, and with Fehling's solution forms a red *copper* derivative. The dark brown, crystalline *copper* derivative, $C_2H_4O_2N_2Cu,2H_2O$, formed by the action of copper acetate on the hydrochloride, decomposes when heated with its mother liquor, yielding nitrogen, nitrous acid, acetic acid, and cuprous chloride. The free *hydroxylamino-oxime* is unstable; on oxidation it yields acetic acid, or with bromine water, ethylnitrosolic acid.

Ethylnitrosolic acid is stable only in its bluish-green solution; it gives a brownish-green coloration with ferric chloride, liberates iodine slowly from acidified potassum iodide solution, and decomposes when warmed. It gives coloured precipitates with salts of the heavy metals in neutral solution; the *silver*, $C_2H_3O_2N_2Ag$, and *potassium* salts are described.

Ethylhydroxyazaurolic acid, $C_2H_8O_3N_4$, crystallises in yellow needles, decomposes at 106—108°, gives with ferric chloride a reddish-brown coloration and Liebermann's nitroso-reaction, and when treated with hydrochloric acid is transformed into the isomeric *azoxy*-compound which immediately decomposes, forming nitrogen and acethydroxamic acid.

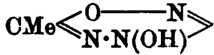
Sodium nitrosoacethydroxylamino-oxime, $C_2H_4O_3N_3Na$, formed by the action of ethylnitrosolic acid on acethydroxylamino-oxime in cooled dilute sodium hydroxide solution, crystallises in nacreous scales, decomposes with detonation above 250°, is decomposed slowly by boiling water, and on acidification yields acethydroxamyl chloride, acethydroxamic acid, and hydroxylamine. The free *nitroso* compound is unstable.

Dibenzoylethylhydroxyazaurolic acid,

$$NO\cdot CMe\colon N\cdot N(OBz)\cdot CMe\colon N\cdot OBz,$$

crystallises in golden needles, m. p. 157° (decomp.), is stable towards aqueous alkalis, but is decomposed by alcoholic alkalis, evolving gas.

Hydroxyleucazone,



$CMe{<}\begin{matrix}O\text{———}N\\ N\cdot N(OH)\end{matrix}{>}CMe$, forms colourless, crystalline, spherical aggregates, m. p. 150° (decomp.), gives a red coloration with ferric chloride, is oxidised by potassium permanganate, forms hygroscopic salts with alkalis and acids, and is stable towards reducing agents, yielding leucazone only in one experiment with stannous chloride and hydrochloric acid. G. Y.

Condensation of Formaldehyde with Hydrazine Hydrate. Robert Stollé (*Ber.*, 1907, **40**, 1505—1507. Compare Pulvermacher, Abstr., 1894, i, 12; Duden and Scharff, Abstr., 1895, i, 122).—This is an account of an unsuccessful attempt to prepare triaminotrimethylenetriamine. The action of 4 mols. of formaldehyde on 5 mols. of hydrazine hydrate leads to the formation of a white, amorphous *product*, which is obtained also when trioxymethylene is heated with hydrazine hydrate under pressure at 100°, and is probably a polymeric *methylenehydrazine*, $(CH_2\colon N\cdot NH_2)_3$ (compare Curtius and Pflug, Abstr., 1892, 456; Curtius and Lublin, Abstr., 1900, i, 700). When heated it detonates without melting, is converted partially into methyleneazine when boiled with water, reacts with benzaldehyde, yielding under certain conditions the mixed aldazine, $CHPh\colon N\cdot N\colon CH_2$, under others, benzylideneazine and methyleneazine, reduces Fehling's and ammoniacal silver nitrate solutions, and with silver nitrate in aqueous solution forms the *additive* compound, $(CH_2\colon N\cdot NH_2)_3,2AgNO_3$, which is obtained as a white powder, detonates when heated, and gradually decomposes, evolving the odour of impure acetamide.

m-Nitrobenzylidenehydrazine (Curtius and Lublin, *loc. cit.*), which is unimolecular, forms an *additive* compound with silver nitrate, $C_7H_7O_2N_3,AgNO_3$; this is obtained as a white, crystalline powder, detonates when heated, and yields the aldazine when suspended in alcohol and treated with hydrogen sulphide. G. Y.

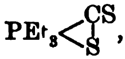
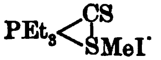
Additive Products of Trialkyl-phosphines, -arsines and -stibines. Arthur Hantzsch and Harold Hibbert (*Ber.*, 1907, **40**, 1508—1519. Compare Hibbert, Abstr., 1906, i, 153).—Co-ordination isomerides, $[RMe_3X]Y$ and $[RMe_3Y]X$, corresponding with hydroxytrimethylammonium bromide and trimethylbromoammonium hydroxide (Abstr., 1905, i, 576), are not obtained if $R = P$, As, or Sb, since these three elements differ from nitrogen in being truly quinquevalent even in their simplest halogen derivatives. The dihaloids and dithiocyanates, RMe_3X_2, behave as salts of very weak bases, being hydrolysed in aqueous solution, not only completely to the hydroxy-salts,

$$OH\cdot RMe_3X,$$

but also further to the hydrate and free acid, $RMe_3(OH)_2$. This hydrolysis is still more marked in the case of the derivatives, SMe_2Br_2 and $OH{\cdot}SMe_2{\cdot}NO_3$, of dimethylsulphoxide, SMe_2O, which is an even more feeble base than are the oxides of trialkyl-phosphines, -arsines or -stibines.

The sulphides of the trialkyl-bases, RMe_3S, form *additive* compounds with methyl iodide, which are most stable in the phosphorus and least so in the antimony series, being hydrolysed by alkalis and water respectively according to the equation $RMe_3S,MeI + H_2O = RMe_3O + HI + SHMe$. The constitution of the phosphorus derivative as a sulphonium, $PMe_3{:}SMeI$, or a phosphonium, $SMe{\cdot}PMe_3I$, compound has not been established.

Contrary to Hofmann's statement (*Proc. Roy. Soc.*, 1860, 10, 186, 616; 1862, 11, 291), the action of tetrachloromethane on triethylphosphine leads to the formation of the derivative $CCl(PEt_3Cl)_3$ only and not to that of the compound, $C(PEt_3Cl)_4$.

The constitution of the red, *additive* compound of triethylphosphine and carbon disulphide is discussed, and the conclusion is drawn that the most probable formula is that suggested by Jacobson,  $PEt_3<\begin{array}{l}CS\\ |\\ S\end{array}$, which represents the substance as an intramolecular anhydride of the acid $OH{\cdot}PEt_3{\cdot}CS{\cdot}SH$, and is in agreement with its conversion by hydrogen chloride into the hygroscopic, colourless chlorotriethylphosphonium dithiocarboxylic acid, $PEt_3Cl{\cdot}CS{\cdot}SH$. This is stable in concentrated acid solution, but is decomposed by water, forming sulphur and hydrogen sulphide. The red, *additive* compound forms a red methiodide in which the ring structure must remain; its constitution is considered to be most probably  $PEt_3<\begin{array}{l}CS\\ |\\ SMeI\end{array}$. The additive compound of triethylphosphine and carbon disulphide is readily decomposed by heating with anhydrous fatty acids, forming triethylphosphine sulphide, carbon oxysulphide, and derivatives of thio-fatty acids.

The additive compounds of the trialkylphosphines and halogens are hygroscopic, and are readily decomposed by water, forming the hydrogen haloid. *Trimethylstibine oxybromide anhydride*, $(SbMe_3Br)_2O$, formed by mixing aqueous solutions of the dibromide and oxide, crystallises in needles. *Trimethylarsine dibromide*, $AsMe_3Br_2$, is obtained by treating the perbromide with acetone.

These dihaloid and oxyhaloid derivatives behave towards sodium hydroxide and phenolphthalein as the free hydrogen haloids. The hygroscopic oxides are neutral to litmus, in agreement with which are the high values obtained for the molecular conductivities of the dihaloid derivatives: trimethylstibine dibromide, $\mu = 500$—521; trimethylarsine dibromide, $\mu = 496{\cdot}8$—$559{\cdot}6$, and trimethylphosphine dibromide, $\mu = 513{\cdot}6$—$565{\cdot}9$, with $v = 64$—1024. As the conductivity of 1 mol. of hydrogen bromide at similar dilutions is $\mu = 402$—406, the hydrolysis of the dihaloid derivatives leads chiefly to the formation of the oxyhaloid compounds, which are hydrolysed to a smaller extent; thus trimethylstibine oxybromide has $\mu = 201{\cdot}2$—$243{\cdot}9$ with $v = 80$—1280.

Trimethylstibine dithiocyanate, $SbMe_3(CNS)_2$, formed by heating the dichloride with potassium thiocyanate in alcoholic solution, is obtained in white crystals.

Triethylphosphine forms unstable *additive* compounds with cyanogen iodide and bromide. The *additive* compound of trimethylstibine and cyanogen iodide, formed in ethereal solution at $-20°$, decomposes readily, and on solution in water or alcohol yields *trimethylstibine oxyiodide*, $(SbMe_3I)_2O$. The colourless *triphenylstibine iodocyanide* is slightly more stable, but decomposes partially even when rapidly dried in a desiccator.

Dimethylsulphide dibromide, SMe_2Br_2, forms yellow crystals; it yields a colourless aqueous solution in which it is completely hydrolysed. The *oxynitrate* has similar properties. The extremely feeble basic properties of dimethylsulphoxide induced the authors to determine the conductivity of solutions of ethylene oxide in hydrochloric acid; the results show that the oxide has no basic properties in aqueous solution.

The sulphides of the trialkyl-phosphines, -arsines, and -stibines are formed by the action of sulphur on the trialkyl bases or by that of hydrogen sulphide on the oxides. *Trimethylstibine sulphide*, $SbMe_3S$, m. p. 168° (decomp.). The methiodides of the sulphides are colourless, neutral salts. *Triethylphosphonium sulphide methiodide*, PEt_3S,MeI, m. p. 123°, is decomposed slowly by boiling water, and is normally dissociated in aqueous solution, having almost the same conductivity as triethylsulphonium iodide, $\mu = 89{\cdot}7 — 105{\cdot}7$, with $v = 32—512$, at 25°. The methiodide is decomposed by alkalis below 0°, the free *base* decomposing immediately into mercaptan and triethylphosphine oxide.

Trimethylarsine sulphide methiodide, $AsMe_3S,MeI$, crystallises in white needles, m. p. about 180° (decomp.), and is decomposed by water. *Trimethylstibine sulphide methiodide* is formed in solution, but cannot be isolated.

The action of carbon tetrabromide on triethylphosphine leads to the formation of *bromomethenyltri-triethylphosphonium bromide*, $CBr(PEt_3Br)_3$. The corresponding chlorine compound is hydrolysed by water, forming chlorotriethylphosphonium chloride, triethylphosphonium oxide, and hydrogen chloride.

The molecular weight of the *additive* compound of triethylphosphine and carbon disulphide, CS_2PEt_3, has been determined cryoscopically in nitrobenzene solution. The *methiodide*, m. p. 96—97°, forms a red, neutral, aqueous solution having the conductivity $\mu_{38} = 93{\cdot}8$, or $\mu_{512} = 98{\cdot}6$, and is decomposed by sodium hydroxide. The free *base* decomposes immediately on liberation, forming mercaptan, sulphur, hydrogen sulphide, triethylphosphonium oxide, and carbon dioxide.

G. Y.

Influence of Solvents in the Claisen Condensation Catalytic Action of Ether and of Tertiary Bases in this Reaction, and also in the Formation of the Grignard Reagent. J. Bishop Tingle and Ernest E. Gorsline (*Amer. Chem. J.*, 1907, 37, 483—494). —The authors have examined the effect of the solvent in the Claisen and Grignard reactions and find a complete parallelism of the two reactions in this respect.

It is possible to accelerate or to retard a given condensation by adding or withdrawing ether from the solution. In the cases examined, the yield of condensation product is essentially the same, whether the sodium compound dissolves in the liquid, is suspended in it, or forms a crust over the sodium wire.

The rapidity with which the magnesium is attacked in the preparation of the Grignard reagent by the halide compound depends on the nature of the alkyl or aryl halide, provided that other conditions remain constant; the presence of ether is not essential to the reaction, nor is a high temperature necessary, provided that sufficient time is allowed. Light petroleum (b. p. 36°) may be used as a solvent. The views of Tschelinzeff regarding the function of the ether in the Grignard reaction are discussed. A. McK.

Conversion of Individual Organo-magnesium Compounds into Amine Complexes and the Thermochemical Investigation of the Reaction. WLADIMIR TSCHELINZEFF (*Ber.*, 1907, **40**, 1487—1496.. Compare Abstr., 1905, ii, 803; 1906, i, 241, 489; ii, 334, 335; this vol., i, 199).—A number of organo-magnesium ammonium compounds have been prepared by various authors by the action of nitrogen compounds on organo-magnesium ether complexes. This method may lead to the formation of mixtures, a disadvantage which is avoided by acting with the amine directly on the individual organo-magnesium compound; this second method has the further advantage that it allows of the preparation of amine complexes having a smaller heat of formation than the corresponding ether complex. In the present paper, the formation of amine complexes, which are considered to have the structure $C_3H_7\cdot Mg\cdot NRR'R''I$ by the action of magnesium propyl iodide on simple aliphatic and aliphatic-aromatic tertiary amines, NRR′R″, is described.

The values found for Q in the thermochemical equation: $NRR'R'' + Mg(C_8H_7)I = NRR'R''I\cdot Mg\cdot C_3H_7 + Q$, are with triethylamine, 11·70 cal.; tripropylamine, 10·32 cal.; tri*iso*amylamine, 9·0 cal.; dimethylaniline, 3·81 cal.; dimethyl-*o*-toluidine, 0·98 cal., and diethylaniline, 0·78 cal. These values are compared with the heats of formation of the corresponding ether complexes formed from magnesium propyl iodide and ethyl ether, 6·63 cal.; ethyl propyl ether, 6·15 cal.; ethyl amyl ether, 5·91 cal., and methyl and ethyl phenoxide, about 0 cal. In agreement with the known properties of ammonium and oxonium compounds, the amine complexes are found to have the greater heats of formation.

G. Y.

Optical Behaviour of Some Styrenes. AUGUST KLAGES (*Ber.*, 1907, **40**, 1768—1772. Compare Abstr., 1904, i, 567).—The refractive indices for H_α, Na, H_β, and H_γ, also N_α, N_{Na}, N_γ, and $N_\gamma - N_\alpha$, as well as the molecular refraction α, Na, γ, and $\gamma - \alpha$, have been measured accurately for a number of styrenes. The calculated molecular refractions and the excess of observed over calculated values are also recorded. For the full details of the physical measurements the original must be consulted.

The homologous series of $\Delta^{\alpha\gamma}$-styrenes all agree in showing an increase in molecular refraction for the red hydrogen and sodium *D* lines of about 4·5 units above the calculated values, and further show an abnormally high dispersion.

α-Phenyl-$\Delta^{\alpha\gamma}$-butadiene (compare von der Heide, Abstr., 1904, i, 583) has D_4^{16} 0·9309, n_{Na}^{16} 1·61283, excess mol. ref$_{Na}$ 4·64.

α-Phenyl-$\Delta^{\alpha\gamma}$-pentadiene, CHPh:CH·CH:CHMe, is a mobile, colourless oil, b. p. 116°/16 mm., m. p. –4°; it polymerises when kept to a viscid liquid, and has D_4^{13} 0·9384, n_{Na}^{13} 1·61114, excess mol. ref$_{Na}$ 4·63. With sodium and boiling ethyl alcohol it yields phenyl-Δ^{β}-pentene, a colourless, fruity oil, b. p. 111°/30 mm., 201°/760 mm.

α-Phenyl-$\Delta^{\alpha\gamma}$-hexadiene, CHPh:CH·CH:CHEt, prepared from magnesium propyl iodide and cinnamaldehyde, contains a carbinol, from which it is freed by treatment with hydrogen chloride and heating with pyridine at 125°. The *hydrocarbon* is a colourless oil, b. p. 128°/16 mm., D_4^{12} 0·9253, n_{Na}^{12} 1·60252, excess mol. ref$_{Na}$ 5·35. On reduction it yields *α-phenyl-Δ^{β}-hexene*, $CH_2Ph\cdot CH:CH\cdot CH_2Et$, b. p. 108°/16 mm., D_4^{16} 0·8898, n_D^{16} 1·5058, mol. ref. 53·4.

α-Phenyl-ε-methyl-$\Delta^{\alpha\gamma}$-hexadiene, $CHPh:CH\cdot CH:CH\cdot CHMe_2$, has b. p. 143°/22 mm., 136°/16 mm., D_4^{20} 0·9248, n_{Na}^{20} 1·58727, excess mol. ref$_{Na}$ 4·66.

α-Phenyl-ζ-methyl-$\Delta^{\alpha\gamma}$-heptadiene, $CHPh:CH\cdot CH:CH\cdot CH_2\cdot CHMe_2$, has b. p. 146—147°/15 mm., D_4^{20} 0·9508, n_{Na}^{20} 1·58547, excess mol. ref$_{Na}$ 3·15.

E. F. A.

Yellow, Red, Green, Violet, and Colourless Salts from Dinitro-compounds. ARTHUR HANTZSCH [and, in part, ERICH BORCHERS, A. H. SALWAY, and E. HEDLEY] (*Ber.*, 1907, 40, 1533—1555).—Whilst the mononitro-compounds, $CH_2R\cdot NO_2$, yield only colourless *aci*-nitro-salts, CHR:NO·OM′, the dinitro-compounds, $CHR(NO_2)_2$, form salts which exist in yellow and red modifications, thus resembling the *chromo*-salts of the nitrophenols and nitro-ketones (compare this vol., i, 513, 555). These yellow and red salts are convertible into each other with varying, but mostly great, ease, depending on the temperature, the solvent, the nature of the metal, and the nature of the dinitro-compound, so that only in a few cases can both modifications be isolated. The aqueous solutions of the yellow and red salts are identical, containing the two forms in equilibrium; at low temperatures the yellow, but at higher temperatures the red, form preponderates. It is shown that the salts are unimolecular in solution and that the degree of dissociation varies with the temperature independently of the change in colour, hence neither form is a polymeride of the other. Since, moreover, both yellow and red salts are obtained in the anhydrous state, the difference in colour must result from isomerism. Coloured ethers of *aci*-dinitroethane have not been obtained.

Dinitroethane on neutralisation behaves as a ψ-acid, the gradual change which takes place in the conductivity of the solutions, formed by mixing dinitroethane and alkalis in molecular proportions, being accompanied by a corresponding change in colour.

The yellow and red salts cannot have the constitution

$$NO_2\cdot CR:NO\cdot OM',$$

since the salts of other *aci*-nitro-compounds, $CRX\colon NO\cdot OM'$, in which $X = Br$ or CN, are colourless, as is also nitrodiazobenzene methyl ether; moreover, under certain conditions, almost colourless salts of *aci*-dinitro-compounds, which are probably colourless salts containing traces of yellow salts and must have the constitution

$$NO_2\cdot CR\colon NO\cdot OM',$$

have been obtained. Hence the constitution of the dinitroethane ion must be changed still further in the yellow and red salts; the constitutions of these and the question as to their structural or stereoisomerism are discussed, but left undecided.

If the two nitro-groups are situated differently in the molecule, as in the nitrophenylnitromethanes, $NO_2\cdot C_6H_4\cdot CH_2\cdot NO_2$, four coloured salts can be formed, yellow and red salts derived from the colourless *aci*-nitro-salt, $NO_2\cdot C_6H_4\cdot CH\colon NO\cdot OM'$, and green and violet salts derived from the colourless *aci*-salt, $OM'\cdot NO\colon C_6H_4\colon CH\cdot NO_2$. Of the colourless salts, only one, the mercuric salt formed from *m*-nitrophenylnitromethane, has been isolated. The stability of the *chromo*-salts depends on the nature of the metal and of the dinitro-compound and on the presence or absence of water of crystallisation; the complete series of four coloured salts has been isolated only in the case of the potassium and cæsium salts of the *p*-nitro-compound.

The ***methyl ether*** of nitrocyanophenylmethane, $CN\cdot CPh\colon NO\cdot OMe$, formed by the action of methyl iodide on the silver derivative at the laboratory temperature, crystallises in colourless needles, m. p. 38—39°, and is hydrolysed only slowly by boiling water, distilling almost unchanged in a current of steam.

The solutions of phenyldinitromethane (Ponzio, Abstr., 1906, i, 735) in non-ionising solvents are colourless, whilst those in alcohol or water are intensely yellow, especially when heated; if an excess of hydrochloric acid is added to the aqueous solution of the alkali salt at 0°, the resulting yellow solution becomes colourless only gradually. The *leuco*-salts have not been isolated in the perfectly colourless state; on addition of a concentrated alkali hydroxide to the finely-powdered dinitro-compound, a colourless salt is formed, but rapidly becomes yellow. On addition of sodium or potassium ethoxide to the alcoholic solution of the dinitro-compound at $-75°$ or at the laboratory temperature, a pale yellow salt is precipitated, sometimes together with the ordinary dark lemon-yellow salt. The aqueous solutions of these pale yellow salts are dark yellow at the ordinary temperature and become red when heated. The lemon-yellow salts form the stable modification at the ordinary temperature. Of the red isomerides, the most stable is the ***sodium*** salt, which is formed from the dinitro-compound by the action of concentrated aqueous sodium hydroxide on the solid, or by addition of sodium ethoxide and ether to the alcoholic solution, or of sodium ethoxide alone to the benzene solution, or from the yellow salt on evaporation of the aqueous solution, or, as green leaflets, by addition of propyl alcohol to the boiling, concentrated solution. It is stable when rapidly dried in presence of ether vapour, but changes into the yellow salt when dissolved, or in contact with the liquids from which it is precipitated, or when acted on by alcohol vapour. When heated with a small amount of alcohol, the yellow salt changes into the red, but is reformed as the alcohol cools. On slow evaporation, the aqueous solution of the yellow salt deposits a mixture of the yellow and red isomerides, occasionally together with the colourless salt. The red salts of the other alkali metals and of ammonium are less stable and, when formed, change rapidly into the yellow modifications.

When freshly prepared, the yellow salts, formed by the action of alkali ethoxides on phenyldinitromethane in ethereal or toluene solution, are much less stable than when obtained from aqueous solutions, and change much more readily into the red modifications at the ordinary temperature; these unstable, yellow salts gradually lose their reactivity, changing into the ordinary, stable, yellow modifications.

The leuco-*potassium* salt of piperonyldinitromethane (Ponzio, *loc. cit.*), $C_8H_5O_6N_2K$, formed by the action of potassium ethoxide on the dinitro-compound in presence of much ether, is straw-coloured, becomes dark-yellow at 60—70°, and dissolves in water, forming the orange solution which is obtained also from the yellow and red *chromo*-salts. The yellow *silver* salt crystallises in orange needles. Of the deep Bordeaux-red salts, the most stable is the *sodium* salt, which when pure remains unchanged for months in a desiccator, and resembles the red salt of phenyldinitromethane. Cryoscopic and ebullioscopic molecular weight determinations show that the pale yellow solution at 0° and the orange solution at 100° contain the normally dissociated, unimolecular salt.

The *lithium* salt ($3H_2O$) of *p*-nitrophenylnitromethane is obtained only in the yellow modification. The *red sodium* salt ($3H_2O$), formed by the action of sodium ethoxide in benzene solution, crystallises in prismatic needles; the *green* isomeride separates from the aqueous solution at $-14°$, and in contact with ice below 0° undergoes transformation into the *yellow* salt ($3H_2O$), which loses $2\frac{3}{4}H_2O$ at 100°, changing into the red salt; this becomes anhydrous at 130°.

The *yellow potassium* salt of *p*-nitrophenylnitromethane ($2H_2O$), formed in aqueous solution at the ordinary temperature, crystallises in leaflets, m. p. 160° (decomp.), and at 100° loses $1\frac{1}{2}H_2O$, changing into the red salt (Holleman, Abstr., 1897, i, 409), which at 130° loses the remaining $\frac{1}{2}H_2O$, forming the *violet* salt. The anhydrous red salt is formed by the action of potassium ethoxide in absolute alcohol on the dinitro-compound in benzene solution. The *green* isomeride ($2H_2O$) is formed when the violet salt or the red salt, obtained from the yellow isomeride by loss of H_2O in a desiccator, is exposed to moist air.

The *rubidium* salt of *p*-nitrophenylnitromethane is formed as the *yellow* modification ($2H_2O$), which loses $2H_2O$ at 100°, yielding the *violet* isomeride; this absorbs $2H_2O$ in moist air, forming the *green* modification. *Yellow* ($2H_2O$), *red* (H_2O), *violet*, and *green cæsium* salts are obtained in a similar manner. *Yellow*, m. p. 136°, and *green ammonium*, and *trimethylammonium*, and *yellow* and *red pyridine* salts are described. The *silver* salt is obtained as a red, gelatinous precipitate, which becomes violet and almost black when dried; the *barium* salt ($2H_2O$) is yellow and loses $1\frac{3}{4}H_2O$ at 120°, becoming red; the *calcium*, *mercurous*, *mercuric*, and *lead* salts are yellow.

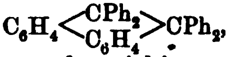
Differently coloured salts, but not differently coloured modifications of the same salt, of *o*-nitrophenylnitromethane have been obtained; the potassium (Holleman, *loc. cit.*) and *sodium*, m. p. 224° (decomp.), salts are red; the *lithium*, *ammonium*, *lead*, *silver*, and *mercuric* salts are yellow; the *mercurous* salt is olive-green. Indications of the formation of a violet potassium salt have been observed.

m-Nitrophenylnitromethane is formed in a 50% yield from *m*-nitrobenzyl chloride and silver nitrite. The alkali salts are orange and are probably mixtures of the yellow and red modifications. The *mercuric* salt, $(NO_2\cdot C_6H_4\cdot CH:NO\cdot O)_2Hg$, is colourless and, in agreement with its formulation as a salt of an oxygen acid, yields mercuric oxide when treated with sodium hydroxide. G. Y.

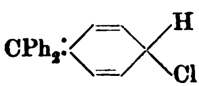
Phenylated Derivatives of 4 : 4′-Ditolyl. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1907, **40**, 1810—1819).—If triphenylmethyl chloride, or its tautomeric modification, has the quinonoid structure ascribed to it by many authors, the first product, $CPh_2:C_6H_5\cdot C_6H_5:CPh_2$, of its reaction with metals should be obtained by isomeric change from bis-4 : 4′-diphenylmethyldiphenyl,

$$CHPh_2\cdot C_6H_4\cdot C_6H_4\cdot CHPh_2.$$

The formation from this of a hydrocarbon, $CPh_2:C_6H_4:C_6H_4:CPh_2$, or



$C_6H_4<\begin{matrix}CPh_2\\C_6H_4\end{matrix}>CPh_2$, by removal of the two methenyl hydrogen atoms, was of special interest, as such a substance would be closely related to Gomberg's triphenylmethyl. In the present paper is described the preparation, by Grignard's reaction from ethyl diphenyl-4 : 4′-carboxylate, of the *glycol*, $OH\cdot CPh_2\cdot C_6H_4\cdot C_6H_4\cdot CPh_2\cdot OH$, the conversion of this into the *dichloride*, $C_{12}H_8(CPh_2Cl)_2$, by the action of hydrogen chloride in glacial acetic acid solution, the reduction of the glycol, by hydriodic acid in glacial acetic acid solution, and of the dichloride, by means of tin and alcoholic hydrochloric acid, forming *bis*-4 : 4′-*diphenylmethyldiphenyl*, and the formation of the *hydrocarbon*, $C_{38}H_{28}$, by the action of zinc, silver, or copper on solutions of the dichloride in an atmosphere of carbon dioxide. The last substance shows its relation, on the one hand, to the diphenyl dyes by the formation of strongly-coloured solutions, and, on the other, to triphenylmethyl by its instability and the ease with which it is oxidised on exposure to air.



The *glycol*, $C_{38}H_{30}O_2$, is purified best by conversion into its dichloride, from which it is regenerated by the action of water in pyridine solution; it crystallises from benzene as a granular powder (C_6H_6), from glacial acetic acid ($2C_2H_4O_2$), from alcohol in small prisms ($2C_2H_6O$), or from a mixture of ethyl acetate and light petroleum as a crystalline powder, which sinters at 160—165°, melts on further heating to a turbid liquid, becoming more opaque, and finally clear at 186—187°. The *dichloride*, $C_{38}H_{28}Cl_2$, crystallises as a white powder, m. p. 219°, and forms a turbid liquid, becoming transparent at 223°; it dissolves in hot acetic acid, forming a light red, or in hot nitrobenzene an intense red, solution, and is readily decomposed by moisture. The *dibromide*, $C_{38}H_{28}Br_2$, formed by the action of hydrogen bromide on the glycol in glacial acetic acid solution, is obtained as a red powder, m. p. 215—219° (decomp.), and is readily decomposed by moisture.

The glycol resembles triphenylcarbinol in forming coloured carbonium salts; similarly coloured compounds are obtained also by the action of zinc, mercuric, and stannic chlorides on the dichloride in nitrobenzene solution. Of these substances, the *compound* with stannic chloride, $C_{38}H_{28}Cl_2,SnCl_4$, has been isolated; it forms a red, amorphous mass, is stable in benzene or hydrochloric acid solution, but is decolorised by dilution with water, and dyes cotton wool in nitrobenzene solution, the dyed cotton wool being more stable towards water than the pure stannichloride.

Bis-4 : 4′-*diphenylmethyldiphenyl*, $C_{38}H_{30}$, crystallises in leaflets, m. p. 162—163°, and yields the above dibromide when acted on by bromine in carbon disulphide solution under the influence of direct sunlight.

The *hydrocarbon*, $C_{38}H_{28}$, separates from a mixture of benzene and light petroleum as a violet powder, is rapidly oxidised by air, especially when moist, and forms solutions resembling those of potassium permanganate; when dissolved in sulphuric acid and treated with water, it yields a white precipitate from which the dichloride is obtained by the action of hydrogen chloride in glacial acetic acid solution.

G. Y.

Chlorination with Phosphorus Pentachloride. LEE H. CONE and C. S. ROBINSON (*Ber.*, 1907, **40**, 2160—2166. Compare Abstr., 1906, i, 424).—Partial replacement of bromine by chlorine occurs when *pp*′-dibromobenzophenone or *p*-bromobenzoic acid is heated with phosphorus pentachloride at 150° for five hours. Benzophenone and *p*-bromobenzophenone retain their nuclei unchanged by treatment with phosphorus pentachloride in hot benzene. Diphenylmethane and phosphorus pentachloride at 170° yield chiefly diphenylchloromethane, while *pp*′-dibromodiphenylmethane at 150° and triphenylmethane at 160° yield respectively *pp*′-*dibromodiphenylchloromethane*, m. p. 92°, and triphenylchloromethane. Phosphorus pentachloride reacts with *ααα*-triphenylethane at 190—200°, forming a monochlorinated product which is probably *ααα-triphenyl-β-chloroethane*, m. p. 118°, with *ααα*-triphenylpropane at 190—200°, yielding in a few minutes *ααα-triphenyl-β-chloropropane* (?), b. p. 240°/47 mm., with *as*-tetraphenylethane at 170—180°, forming *tetraphenylethylene*, m. p. 221° (the *s*-isomeride is not attacked at 190°), and with pentaphenylethane at 170°, yielding triphenylchloromethane as the only crystalline product isolated.

C. S.

Triphenylmethyl. XVI. Tautomerism in the Triphenylmethane Series. MOSES GOMBERG (*Ber.*, 1907, **40**, 1847—1888. Compare Abstr., 1906, i, 822).—Triphenylmethyl chloride and its derivatives react with silver sulphate in benzene solution, forming coloured solutions and yielding the theoretical amounts of silver chloride. Whilst, under the same conditions, *o*-bromo-, and *m*-bromotriphenylmethyl chlorides yield only 1 mol. of silver chloride, the amount of silver haloid, obtained from tri-*p*-chloro-, tri-*p*-bromo-, and 2 : 4′ : 4″-trichlorotriphenylmethyl chlorides, shows that one nucleus halogen atom has been removed in addition to the chlorine of the carbinyl chloride group. This reaction takes place only partially at 20°, probably in consequence of the protection of the silver sulphate by a layer of insoluble carbinyl sulphate, more nearly quantitative results being obtained on prolonged shaking at 50°. The nucleus halogen atom reacts only when in the para-position and after formation of the carbinyl sulphate; tri-*p*-chlorotriphenylmethyl ethyl ether does not react with silver sulphate. It is argued that all coloured substances of the triphenylmethane series, and therefore the triphenylmethyl sulphates, are quinones, and that the nucleus halogen atom can react with silver sulphate only when the substance is in the quinonoid form. On hydrolysis, the red *sulphate*, formed from *p*-bromotriphenylmethyl chloride, yields a yellow, crystalline *substance* having a pronounced odour of quinone. The *sulphate*, obtained from tri-*p*-bromotriphenylmethyl chloride, separates from methyl sulphate in red crystals, m. p. 135—136°, probably contains methyl sulphate of crystallisation, and when shaken with ether and water loses sulphuric acid and forms a red, amorphous *mass*, which may be *di*-p-*bromodiphenylquinomethane*, $C_6H_4O\colon C(C_6H_4Br)_2$.

The acid sulphates, formed by the action of an excess of methyl sulphate on tri-*p*-bromo- and tri-*p*-chloro-triphenylmethyl chlorides, vary in composition between $CR_3\cdot SO_4H,1\frac{1}{2}H_2SO_4$ and

$$CR_3\cdot SO_4H,2H_2SO_4,$$

form small, red, strongly hygroscopic crystals, are iridescent by reflected light, are insoluble in benzene, and in agreement with von Baeyer's statement (Abstr., 1905, i, 281) do not react with silver sulphate or molecular silver. The results of experiments with *p*-bromo- and tri-*p*-bromo-triphenylmethyl chlorides are quoted, showing that whilst the carbinyl chloride reacts with silver sulphate quantitatively even in presence of two and two-third mols., the reaction of the nucleus halogen atom is hindered by the presence of less than 1 mol. of free sulphuric acid, which acts as a negative catalyst. The reaction with silver sulphate is hindered similarly by the presence of sulphur dioxide. In both cases the action of the monobromo-compound is more readily affected than that of the tribromo-compound by the negative catalyst.

All triphenylmethylcarbinyl chlorides, although colourless when solid, form yellow to red solutions in liquid sulphur dioxide, the colourless chlorides being regained on evaporation. If coloured substances of the series have quinonoid structures, the solutions of the carbinyl chlorides in liquid sulphur dioxide should behave differently to the colourless solutions in solvents such as benzene. This is found to be the case in the behaviour of the *p*-bromo-derivatives towards silver chloride; in liquid sulphur dioxide solution the nucleus bromine is substituted by chlorine, silver bromide being formed, whilst the reaction takes place to only a small extent in methyl sulphate and not at all in benzene or toluene solution. The tautomerising effect of the sulphur dioxide is diminished by dilution of the solution with methyl sulphate or, to a still greater extent, with toluene. 4 : 4′-*Dichloro-*4″*-bromotriphenylmethyl chloride*, $C_{19}H_{12}Cl_3Br$, formed by the action of silver chloride on tri-*p*-bromotriphenylmethyl chloride dissolved in a mixture of toluene and liquid sulphur dioxide, or from ethyl *p*-bromobenzoate and *p*-chloroiodobenzene by Grignard's reaction, crystallises in white needles, m. p. 122°. Tri-*p*-chlorotriphenylmethyl chloride is formed by the action of an excess of silver chloride on tri-*p*-bromo-, 4-*chloro*-4′ : 4″*-dibromo*-, m. p. 133°, and 4 : 4′-dichloro-4″-bromotriphenylmethyl chlorides in liquid sulphur dioxide. The whole reaction may be represented as taking place in stages in the following manner: $C(C_6H_4Br)_3Cl \longrightarrow C_6H_4BrCl{:}C(C_6H_4Br)_2 \longrightarrow$

$C_6H_4Cl_2{:}C(C_6H_4Br)_2 \longrightarrow$

$C_6H_4Cl{\cdot}C(C_6H_4Br)_2Cl \longrightarrow C_6H_4Cl{\cdot}C(C_6H_4Br){:}C_6H_4BrCl \longrightarrow$, &c. The benzenoid compound, $C_6H_4Cl{\cdot}C(C_6H_4Br)_2Cl$, must be formed, even if only in small amount, in equilibrium with the preceding, as also with the succeeding, quinonoid substance.

The second half of this paper contains a long, theoretical discussion of the basic properties of carbon and of the constitution of the triphenylmethane dyes and of triphenylmethyl. G. Y.

Catalysis: Rearrangement of Acetylhalogenaminobenzene Derivatives into Halogen Acetanilide Derivatives. Salomon F. Acree and J. M. Johnson (*Amer. Chem. J.*, 1907, **37**, 410—413).—It has been shown by Blanksma (Abstr., 1902, ii, 646) that the velocity of the rearrangement of acetylphenylchloroamine into *p*-chloroacetanilide in presence of hydrochloric acid is that of a unimolecular reaction, and increases as the square of the concentration of the acid increases.

It is now found that the catalytic action of the acid is not due to the hydrogen ions present, but that an intermediate compound is produced, thus: $CH_3{\cdot}CO{\cdot}NPhCl + HCl \longrightarrow CH_3{\cdot}CO{\cdot}NHPhCl_2 \longrightarrow CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4Cl + HCl$. Acetylphenylchloroamine and hydrobromic acid yield *p*-bromoacetanilide; acetylphenylbromoamine and hydrochloric acid yield the same product, owing to the fact that the bromine migrates to the benzene nucleus more rapidly than chlorine. Chlorine and bromine quickly convert acetylphenylchloroamine into *p*-chloroacetanilide and *p*-bromoacetanilide respectively. The reaction between acetylphenylchloroamine and hydrobromic acid is of the second order, and the velocity constant of the rearrangement is about one thousand times as great as that induced by hydrochloric acid of the same concentration. It is evident that the catalysis is not directly dependent on the concentration of the hydrogen ions, and it is shown from a consideration of the mass law that the phenomena are easily explained on the hypothesis of the formation of an intermediate compound. Since, in this case, the velocity of the reaction is not proportional to the concentration of the hydrogen ions of the catalysing agent, but to the square of that concentration, it seems possible that there may be reversible actions in which the equilibrium is changed by a change in the concentration of the catalyser. The energetic catalytic action of chromium nitride in effecting its own formation from chromium and ammonia, whilst it has no great influence in the reverse reaction, namely, the formation of ammonia from its elements (Baur and Voerman, Abstr., 1905, ii, 715), is regarded as a case of this kind.

E. G.

Preparation of Acyl Alkyl Compounds of Highly Halogenated Aromatic Amines. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 180203, 180204).—The acyl derivatives of highly chlorinated aromatic amines are readily obtained by heating the sodium derivative of the acylated base with an alkyl haloid.

Aceto-2 : 3 : 4 : 6-*tetrachloroethylanilide*, m. p. 73—74°, is produced by heating aceto-2 : 3 : 4 : 6-tetrachloroanilide with alcoholic sodium ethoxide and ethyl chloride for twenty-four hours at 100°.

Aceto-2 : 3 : 4 : 6-*tetrachloromethylanilide*, m. p. 96—97°, *aceto*-2 : 3 : 4 : 6-*tetrachlorobenzylanilide*, m. p. 97°, and *benzo*-2 : 3 : 4 : 6-*tetrachlorobenzylanilide*, m. p. 134°, are similarly prepared, and are employed as camphor substitutes in the production of celluloid.

The primary aromatic amines, containing halogen atoms in both the contiguous ortho-positions with respect to nitrogen, are acylated only with difficulty, but the corresponding monoalkyl derivatives readily undergo condensation with acid chlorides or anhydrides.

Aceto-2 : 4 : 6-*trichloromethylanilide*, m. p. 89—90°, is readily obtained by heating 2 : 4 : 6-trichloromethylaniline with glacial acetic acid and acetyl chloride.

The employment of ethyl- and benzyl-2 : 4 : 6-trichloroanilines leads to the formation of *aceto*-2 : 4 : 6-*trichloroethylanilide*, m. p. 50—51°, and *aceto*-2 : 4 : 6-*trichlorobenzylanilide*, m. p. 61°. These condensations occur even more smoothly with acetic anhydride.

Benzo-2 : 4 : 6-*trichloroethylanilide*, m. p. 127—128°, is obtained by gradually heating to 150° a mixture of 2 : 4 : 6-trichloroethylaniline and benzoyl chloride.

G. T. M.

Nitrogen Derivatives of Trichloroacetic Acid. LEOPOLD SPIEGEL and PERCY SPIEGEL (*Ber*, 1907, 40, 1730—1740).—Ethyl trichloroacetate is conveniently prepared by passing hydrogen chloride into a cooled molecular mixture of alcohol and the acid. *Trichloroaceto*-p-*phenetidide*, $OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CCl_3$, forms colourless, rhombic plates, m. p. 132°; the *methylanilide* forms colourless needles, m. p. 55°; the p-*nitroanilide*, $C_6H_4(NO_2)\cdot CO\cdot CCl_3$, separates in almost colourless, prismatic columns, m. p. 147°, whilst the o-*nitroanilide* yields long, yellow needles, m. p. 65°. *Bis-trichloroacetyl*-p-*phenylenediamine*, $C_6H_4(NH\cdot CO\cdot CCl_3)_2$, crystallises in colourless, glistening plates, m. p. 264° (decomp.), whilst the o-*phenylenediamine* derivative gives well-formed, colourless needles, m. p. 233—234° (browning and decomposition). On prolonged heating at 200°, part of the substance decomposes and part sublimes in long, silky, glistening needles. o-*Trichloroacetylaminophenol*, $OH\cdot C_6H_4\cdot NH\cdot CO\cdot CCl_3$, forms colourless, silky, glistening needles, m. p. 161—162°. o-*Trichloroacetylaminophenyl benzoate*, $OBz\cdot C_6H_4\cdot NH\cdot CO\cdot CCl_3$, forms colourless, brightly glistening, rhombic plates, m. p. 104—105°. *Bis-trichloroacetylhydrazine*, $N_2H_2(CO\cdot CCl_3)_2$, crystallises in colourless, quadrate pyramids, m. p. 195°; *trichloroacetyl-*

p-*nitrophenylhydrazine*, $NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot CO\cdot CCl_3$, prepared by heating the hydrazine in ethereal suspension with trichloroacetyl chloride, gives bright red needles from alcohol and orange-red, hexagonal plates from benzene, both of which become reddish-yellow on standing in a vacuum; m. p. 164° (decomp.). The compound colours the skin an intense reddish-yellow and forms a very delicate indicator for alkali.

β-Benzoyl-α-trichloroacetylhydrazine, $NHBz\cdot NH\cdot CO\cdot CCl_3$, crystallises in large, glistening plates, m. p. 168°. *Trichloroacetylcarbamic hydrazide*, $NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot CCl_3$, forms small, colourless, quadrate columns, m. p. 175°. *β-Benzoyl-α-trichloroacetyl-α-phenylhydrazine*, $NHBz\cdot NPh\cdot CO\cdot CCl_3$, crystallises in glistening, colourless needles, m. p. 178°. E. F. A.

α-Anilino*iso*butyronitrile and Derivatives. A. Mulder (*Rec. trav. chim.*, 1907, **26**, [ii], 180—187).—Tiemann and Stephan have stated (Abstr., 1883, 199) that the product obtained by the condensation of aniline with acetonecyanohydrin is α-anilino*iso*butyronitrile, and that the acid and amide obtained from it by hydrolysis are also α-derivatives. Bischoff and Mintz, on the contrary (Abstr., 1892, 1338), have found that aniline condenses with ethyl α-bromo*iso*butyrate to furnish ethyl β-anilino*iso*butyrate, and the acid and amide obtainable from this being identical with those prepared by Tiemann from his nitrile, they suggested that the latter must be a β-derivative. The author finds that Tiemann's nitrile, on reduction with sodium in boiling alcohol, furnishes *iso*propylaniline and is therefore an α-derivative, and infers that if the acid and amide prepared by Bischoff and Mintz are β-derivatives (compare Bucherer and Grolée, Abstr., 1906, i, 349), transposition must occur, probably during the hydrolysis of the nitrile to the amide. Acetonecyanohydrin does not condense with methylaniline.

When α-anilino*iso*butyronitrile is gradually mixed with excess of nitric acid (D 1·4) and the mixture heated to boiling, it furnishes the 2 : 4-*dinitro*-derivative, m. p. 157°, which crystallises from acetic acid in yellow spangles and is decomposed by sulphuric acid, yielding 2 : 4-dinitroaniline and 2 : 4-*dinitroanilino*iso*butyramide*, m. p. 155—156°, which may also be obtained by direct nitration of the amide prepared by Tiemann's method (*loc. cit.*). It crystallises from alcohol in yellow plates. When heated with hydrochloric acid at 100°, the nitrile yields the corresponding *dinitro-acid*, m. p. 190—191° (decomp.), which separates from dilute acetic acid in small, bright yellow crystals together with a small amount of 2 : 4-dinitroaniline.

When anilino*iso*butyramide, obtained by Tiemann's method, is dissolved in hydrochloric acid and an aqueous solution of sodium nitrite is added, *phenylnitrosoamino*iso*butyric acid*, m. p. 141—142°, is obtained, which crystallises from water in colourless needles, gives the Liebermann reaction, and regenerates the amide on reduction with tin and hydrochloric acid. T. A. H.

Hexahydroaromatic Amines. Johannes Gutt (*Ber.*, 1907, **40**, 2061—2070).—The author has prepared and characterised the five possible isomeric amines of methyl*cyclo*hexane. The optical properties of the new substances described are fully given in each case as well as those of a number of others. β-Methyl*cyclo*hexanol yields a chloride convertible into hexahydro-*m*-toluic acid, the chloride of which with aqueous ammonia forms 3-amino-1-methyl*cyclo*hexane. This has $[\alpha]_D$ −1·9°, D_4^{20} 0·8456, b. p. 150°/747 mm.; the *urethane* has b. p. 123°/12 mm., m. p. 60—61°; the *N*-benzoyl derivative forms long needles, m. p. 163° (corr.).

1-Methyl-2-*cyclo*hexanol was converted into hexahydro-*m*-toluic acid, of which the *chloride* has b. p. 75—76°/15 mm. and the *amide*, m. p. 180°. 2-*Amino*-1-*methyl*cyclo*hexane* has b. p. 149°/760 mm., D_4^{21} 0·8558; the *urethane*, b. p. 123°/14 mm., m. p. 76—77°; *aurichloride*, yellow needles, m. p. 205—207°, and *N-benzoate*, flat needles, m. p. 146—147°, are described.

The *amide* of hexahydro-*p*-toluic acid has m. p. 220—221° (corr.); the *urethane* derived from it shows b. p. 138°/21 mm., m. p. 76°. 4-*Amino*-1-*methyl*cyclo*hexane* has b. p. 150°/743 mm., D_4^{20} 0·8472; the *hydrochloride*, glistening plates, m. p. 260°; *aurichloride*, m. p. 189°; *platinichloride*, m. p. 260° (decomp.), and *N-benzoate*, glistening, flat needles or plates, m. p. 180°, are described.

Hexahydrobenzylamine has b. p. 163·5°/760 mm. (corr.), D_4^{20} 0·8702, and forms an *aurichloride*, m. p. 183°; *platinichloride*, m. p. above 280° (decomp.), and an *N-benzoate*,' m. p. 107°. The *urethane* has b. p. 140°/15 mm. and m. p. 35°. 1-Amino-1-methyl *cyclo*hexane has b. p. 142° (750 mm.), D_4^{20} 0·8565, and forms a *benzoate*, m. p. 101°.

E. F. A.

Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. IV. Hans Th. Bucherer and Franz Seyde (*J. pr. Chem.*, 1907, [ii], 75, 249—293. Compare Abstr., 1903, i, 627; 1904, i, 309, 395; 1905, i, 48, 585).—It has been shown in previous communications that primary and secondary aliphatic amines can be prepared by alkylation and decomposition of the resulting secondary or tertiary amine by means of sodium hydrogen sulphite, the process being rendered in a sense continuous by conversion of the phenol or naphthol, formed together with the aliphatic amine, into the original aromatic amine. In the present paper, the preparation of benzylamine and of diethylenediamine (piperazine), and unsuccessful attempts to prepare dibenzylamine by this series of reactions are described. It is found that sodium naphthionate reacts easily with 1 mol. of benzyl chloride in sodium carbonate solution, forming α-benzylaminonaphthalene-4-sulphonic acid together with small amounts of benzyl alcohol, or in sodium acetate solution together with traces of dibenzyl-α-naphthylamine. 2-Benzylaminonaphthalene-4-sulphonic acid is decomposed by sodium hydrogen sulphite solution, slowly at the temperature of the water-bath, or more quickly at 125° under pressure, benzylamine hydrochloride being formed in a 70% yield. Prolonged action of an excess of benzyl chloride on naphthionic acid in boiling aqueous sodium acetate solution leads to the formation of a mixture of α-benzylamino- and α-dibenzylamino-naphthalene-4-sulphonic acids together with dibenzyl-α-naphthylamine in a yield of 4·5% of the naphthionic acid

The dibenzylamino-sulphonic acid could not be isolated; the mixture of benzylated amino-sulphonic acids, when boiled with aqueous sodium hydrogen sulphite, yields 12% of benzylamine, the dibenzyl compound remaining undecomposed by the sulphite even at 150°.

Similar results are obtained on benzylating α-naphthylamine-4 : 7-disulphonic and α-naphthylamine-4 : 8-sulphonic acids. Of the mono- and dibenzyl derivatives, only sodium hydrogen α-benzylaminonaphthalene-4 : 8-disulphonate has been isolated. Benzylamine is formed in 77·4%, 74·4%, and 20·3% yields from the solutions obtained by the action of 1 mol. of benzyl chloride on the 4 : 7- and 4 : 8-disulphonic acids and of 2 mols. of benzyl chloride on the 4 : 8-disulphonic acid respectively.

Naphthionic acid does not form a piperazine derivative with ethylene dibromide, whilst in consequence of its insolubility, di-α-naphthylpiperazine (Abstr., 1889, 1011) does not react with sodium hydrogen sulphite, but when rendered soluble by sulphonation it is decomposed to a small extent by the sulphite at 140—160°, yielding piperazine and a naphtholsulphonic acid.

It was observed (Abstr., 1905, i, 48) that the yields obtained in the preparation of secondary arylamines from derivatives of β-naphthol with anthranilic, sulphanilic, or metanilic acid by the sodium hydrogen sulphite method were the poorer the more soluble the product. In agreement with this, β-naphthol-6 : 8-disulphonic and β-naphthol-6-sulphonic acids are found to condense readily with *p*-phenylenediamine and *p*-aminophenol, whilst β-naphthol-3 : 6-disulphonic acid does not react with *p*-phenylenediamine or aniline in presence of sodium hydrogen sulphite. 2-Hydroxy-3-naphthoic acid and 2 : 8-dihydroxy-6-sulpho-3-naphthoic acid enter into the reaction more readily than does β-naphthol. It is found, further, that better yields are obtained by the action of derivatives of β-naphthol with *p*-substituted than with *o*-substituted arylamines, and that whilst β-hydroxynaphthoic acids are decomposed readily with loss of carbon dioxide, their esters remain unchanged on prolonged boiling with aqueous sodium hydrogen sulphite; in consequence of this stability of the carbethoxy-group, the esters of β-hydroxynaphthoic acids do not form amines by the sulphite reaction.

The constitutions of 2 : 8-dihydroxynaphthalene-6-sulphonic and 8-hydroxy-2-naphthylamine-6-sulphonic acids, formed by fusion of *G* salt and of amino-*G* salt respectively, are confirmed by the formation of these acids from nigrotic acid (2 : 8-dihydroxy-6-sulpho-3-naphthoic acid) by boiling with sodium hydrogen sulphite solution and by heating with ammonium sulphite and ammonia at 150° under pressure.

α-Benzylaminonaphthalene-4-sulphonic acid, $C_{17}H_{15}O_3NS$, crystallises from water in yellowish-white needles or separates as an amorphous powder; the *sodium* salt crystallises in white needles and has a blue fluorescence in dilute, aqueous solution.

Dibenzyl-α-naphthylamine, $C_{24}H_{21}N$, crystallises from alcohol in white needles, m. p. 108°, and has a blue fluorescence in alcoholic solution; the *hydrochloride*, $C_{24}H_{21}N,HCl$, a white powder, m. p. 186°, decomposed by water.

Sodium hydrogen a-benzylaminonaphthalene-4 : 8-*disulphonate*,

$C_{17}H_{14}O_6NS_2Na$,

forms microscopic needles.

β-p-*Aminophenylaminonaphthalene*-6 : 8-*disulphonic acid*,

$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_{10}H_5(SO_3H)_2$,

formed from *β*-naphthol-6 : 8-disulphonic acid and *p*-phenylenediamine, crystallises in yellow, microscopic needles; the *sodium hydrogen* salt, $C_{16}H_{13}O_6N_2S_2Na$, was analysed.

β-p-*Hydroxyphenylaminonaphthalene*-6 : 8-*disulphonic acid*, from *β*-naphthol-6 : 8-disulphonic acid and *p*-aminophenol, crystallises in yellowish-white needles; the *sodium hydrogen* salt, $C_{16}H_{12}O_7NS_2Na$, was analysed.

The analytical results obtained with the product of the condensation of *β*-naphthol-6-sulphonic acid and *p*-phenylenediamine point to the presence of a mixture of disulphonaphthyl-*p*-phenylenediamine and bisdisulphonaphthyl-*p*-phenylenediamine.

β-p-*Acetylaminophenylaminonaphthalene*-6-*sulphonic acid*, formed together with a small amount of a sulphur-free *compound*, crystallising in microscopic rhomboids, was isolated in the form of its *sodium* salt, $C_{18}H_{15}O_4N_2SNa$, which is obtained as a bluish-white, crystalline powder.

The following new *β*-naphthylamines, $C_{10}H_7{\cdot}NHR$, are formed by condensation of aromatic amines, NH_2R, with 3-hydroxy-2-naphthoic acid in sodium hydrogen sulphite solution.

$R=C_6H_4Me$ (*m*): white needles, m. p. 67—68°, has a blue fluorescence in alcoholic solution; $R=C_6H_3Me_2(Me_2=2:4)$: transparent prisms, m. p. 40°; $R=C_6H_4{\cdot}OMe$ (*p*): rhombic leaflets, m. p. 104°; $R=C_6H_4{\cdot}OMe$ (*o*): leaflets, m. p. 68°; $R=C_6H_4{\cdot}OEt$ (*p*): white leaflets, m. p. 95°, has a blue fluorescence in alcoholic solution; $R=C_6H_4{\cdot}NH_2$ (*m*): red, crystalline powder, m. p. 95°, forms a *monohydrochloride*, m. p. 205° (decomp.); $R=C_6H_4{\cdot}NH_2$ (*p*): slender needles, m. p. 94°, has a blue fluorescence in alcoholic solution, and forms a *monohydrochloride*, white needles, m. p. about 240° (decomp.), and a *dihydrochloride*, m. p. 240° (decomp.), which becomes green, and has a blue fluorescence in alcoholic solution; $R=C_6H_4{\cdot}NHAc$ (*p*): m. p. 160°. *Di-β-naphthyl*-p-*phenylenediamine*, $C_6H_4(NH{\cdot}C_{10}H_7)_2$, formed in small quantity together with the mononaphthyl compound, crystallises in white needles, m. p. 228°; $R=C_6H_4{\cdot}CO_2H$ (*o*): needles, m. p. 208°, is formed together with $R=Ph$ from anthranilic acid; $R=C_6H_3(OH){\cdot}CO_2H$ $[OH:CO_2H=4:3]$: tetragonal leaflets, m. p. 176°; $R=C_6H_4{\cdot}SO_3Na$ (*m*): white, prismatic needles, forms a sparingly soluble *copper* salt; $R=C_6H_4{\cdot}SO_3Na$ (*p*): white, crystalline powder, forms a green *copper* salt. The *condensation* product of 3-hydroxy-2-naphthoic acid with pararosaniline is a mixture of mono- and dinaphthyl compounds, forms an insoluble, bluish-violet powder or green crystals, dissolves in concentrated sulphuric acid to a reddish-brown solution becoming blue on dilution, and dyes wool violet-blue. The condensation of 3-hydroxy-2-naphthoic acid with safranine leads to the formation of a mixture of *mono*- and *di-naphthyl* derivatives of safranine, which forms a green, crystalline mass, and dyes wool bluish-violet.

2-p-*Tolylamino*-8-*naphthol*-6-*sulphonic acid*, $C_{17}H_{15}O_4NS$, is formed in small amount by the condensation of *p*-toluidine with nigrotic acid; it is obtained in microscopic needles.

The action of ammonium sulphite and concentrated ammonia on ethyl 3-hydroxy-2-naphthoate in a sealed tube at 125° leads to the formation of 3-hydroxy-2-naphthoamide, m. p. 215—216° (185^{c}: Rosenberg, Abstr., 1893, i, 221).

Technical nigrotic acid must contain 6-sulpho-β-naphthol-3-carboxylic acid, since the formation from it of 2:8-dihydroxynaphthalene-6-sulphonic acid is accompanied by that of β-naphthol-6-sulphonic acid and the formation of 8-hydroxy-β-naphthylamine-6-sulphonic acid by that of β-naphthylamine-6-sulphonic acid. The 6-sulpho-β-naphthol-3-carboxylic acid cannot be removed completely by conversion of the nigrotic acid into its toluidine salt. G. Y.

Action of Bases, Ammonia, and Amines on *s*-Trinitrophenylmethylnitroamine. PIETER VAN ROMBURGH and A. D. MAURENBRECHER (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, 9, 704—706).—When *s*-trinitrophenylmethylnitroamine is boiled with a 10% solution of potassium carbonate, the solution cooled, acidified, and extracted with ether, methylnitroamine is obtained, but the yield is very small. If 20% methyl- or ethyl-alcoholic ammonia is used instead of aqueous potassium carbonate, the yield is 15%, but the best result is obtained when *p*-toluidine dissolved in 96% ethyl alcohol is employed. By this method, 7 grams of methylnitroamine were obtained from 35 grams of the trinitrophenyl derivative. H. M. D.

Asymmetric Nitrogen. XXIX. Resolution of Phenylbenzylmethylbutylammonium Compounds. EMANUEL FRÖHLICH and EDGAR WEDEKIND (*Ber.*, 1907, 40, 1646—1650. Compare this vol., i, 409, 410).—*Methylbutylaniline*, $NMeBu^{a}Ph$, b. p. 240—244°, is best obtained by warming methylaniline with successive small quantities of butyl iodide, the basic mixture being separated after each addition of the iodide. The base and benzyl iodide yield crystals of *phenylbenzylmethylbutylammonium iodide*, m. p. 140—141° (decomp.): The corresponding *bromide* has m. p. 157—158° (decomp.). The d-*camphorsulphonate*, m. p. 159° (decomp.), is fractionated in chloroform solution by the addition of ether, the twenty-seventh fraction giving a constant value of $[M]_D^{20}$ −202·1°, which leads to the value $[M]_D^{20}$ −253·8° for the *l*-ammonium ion. *l*-Phenylbenzylmethylbutylammonium iodide has $[M]_D^{20}$ −319·6° in alcohol and −346·1° in chloroform; the substance undergoes autoracemisation in the latter solvent, but at a much smaller velocity than in the case with the isomeric *iso*butyl compound. C. S.

Diphenylcarbamyl Chloride as a Reagent for Phenols. JOHANNES HERZOG (*Ber.*, 1907, 40, 1831—1834. Compare Abstr., 1905, i, 804; Erdmann and Huth, Abstr., 1896, i, 198; 1896, i, 35;

Erdmann, Abstr., 1902, i, 553).—All phenols and derivatives of phenols, excepting the carboxylic acids, react readily with diphenylcarbamyl chloride in boiling pyridine solution, forming diphenylurethanes of the type $NPh_2 \cdot CO \cdot OPh$ in 70—90% yields. The reaction of the esters of aromatic hydroxy-carboxylic acids is irregular and requires further investigation.

In the absence of a phenol, diphenylcarbamyl chloride reacts with pyridine, forming *diphenylcarbamylpyridine chloride*,

$$C_5H_5NCl \cdot CO \cdot NPh_2,$$

which crystallises in colourless needles, m. p. 110° (decomp.), becomes red on exposure to light, is decomposed by water, and reacts with phenols, forming urethanes.

The following urethanes, derived from the phenols mentioned, are described; $R = \cdot CO \cdot NPh_2$. Phenol, $R \cdot OPh$, m. p. 104—105; resorcinol, $C_6H_4(OR)_2$, m. p. 129—130°; pyrogallol, $C_6H_3(OR)_3$, m. p. 211·5—212·5°; *o*-cresol, $C_6H_4Me \cdot OR$, m. p. 72—73°; *m*-cresol, m. p. 100—101·5°; *p*-cresol, m. p. 93—94°; *o*-nitrophenol, $NO_2 \cdot C_6H_4 \cdot OR$, m. p. 113·5—114·5°; *o*-aminophenol, $NH_2 \cdot C_6H_4 \cdot OR$, becomes yellow at 173°, m. p. 177°; *β*-naphthol, $C_{10}H_7 \cdot OR$, m. p. 140·5—141·5°; eugenole, $C_{10}H_{11}O \cdot OR$, m. p. 107—108°; salol, $C_{13}H_9O_2 \cdot OR$, m. p. 143—144·5°.

As these urethanes are readily hydrolysed by alcoholic potassium hydroxide at 100°, they may be employed in the purification as well as in the identification of phenols. G. Y.

Constitution and Colour of Nitrophenols, and especially of Nitroquinol Dimethyl Ether. Arthur Hantzsch (*Ber.*, 1907, 40, 1556—1572. Compare Hantzsch, Abstr., 1906, i, 353, 833; Ley and Hantzsch, *ibid.*, 790).—A reply to Kauffmann (this vol., i, 127). The assumption that the formation of coloured ions from colourless substances is the result of a change in chemical structure is justified by the close resemblance of the yellow and red salts of the nitrophenols to the yellow and red salts of the dinitro-compounds (compare this vol., i, 500, 555). The relation between the affinity constants of nitrophenols and the hydrolysis of their salts follows from the data given by Praetorius (*Diss.*, 1902); *p*-nitrophenyl has the conductivity $\mu_{50} = 0{\cdot}69$, from which the affinity constant $K = 735 \cdot 10^{-10}$, and the degree of hydrolysis of the sodium salt, 0·23% with $v = 32$, are calculated; similarly, *o*-nitrophenol has the conductivity $\mu_{165} = 1{\cdot}08$, the affinity constant $K = 557 \cdot 10^{-10}$, and the degree of hydrolysis of the sodium salt, 0·26°/o with $v = 32$. The degree of hydrolysis of the sodium salt, as determined by Shield's methyl acetate method, with $v = 32$, is for *p*-nitrophenol, 0·28°/o, and for *o*-nitrophenol, 0·26°/o.

Molecular weight determinations of nitroquinol dimethyl ether show that, contrary to Kauffmann's assumption, both the solution in methyl alcohol, which is intensely yellow, and that in hexane, which is almost colourless, contain the unimolecular ether. The molecular weight increases with the concentration of the hexane, but not with that of the methyl-alcoholic solution, which points to the formation of association products in the yellow solutions. In its yellow solutions, nitroquinol dimethyl ether behaves as a non-electrolyte.

Solutions of nitroquinol dimethyl ether in a number of solvents have been examined by means of Martens-Grünbaum's spectrophotometer, and are arranged according to the intensity of colour in the following order: sulphuric acid, water, methyl and ethyl alcohols, ethyl acetate, propyl butyrate, benzene, and hexane; the colour intensity of the solution in methyl alcohol is 20, in water 200, and in sulphuric acid almost 500 times that of the solution in hexane. The colour intensity is shown to increase with the dielectric constant of the solvent; this is still more marked, although more irregular, in the case of solutions in unsaturated (allyl alcohol and pentene) and halogen (chlorobenzene, chloroform, carbon tetrachloride, and bromoform) compounds. A similar relation between the dielectric constant of the solvent and the colour intensity of the solution is observed in the case of other aromatic nitro-compounds.

p-Nitroanisole, after repeated recrystallisations, forms solutions in methyl alcohol and ethyl acetate, which appear colourless and do not absorb blue, but absorb violet, rays when concentrated. Nitrobenzene absorbs rays in the extreme violet, and forms colourless solutions therefore only in solvents with small dielectric constants. It is unimportant, consequently, whether such nitro-compounds are termed coloured or colourless; of importance is that these true nitrophenol ethers are "practically colourless" in comparison with the intensely coloured *chromo*-salts and *chromo*-ethers.

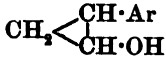
[With KURT MEISENBURG.]—In agreement with the results of the colorimetric investigation, it is found that the molecular refraction of aromatic nitro-compounds in various solvents agrees the more closely with the values calculated or determined with the undiluted, liquid substance the more indifferent the solvent. In the experiments described, the optical effects of the solvent have been eliminated by employing only solvents having similar refractive indices and dispersions: methyl alcohol, acetone, chloroform, *iso*butyl butyrate, and hexane; the molecular refractions in the first two, strongly dissociating, are compared with those in the three indifferent solvents. The molecular refractions have been determined for the following substances; the values given are the differences between the calculated molecular refractions and those found in the solvents named at 20°.

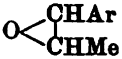
Anisole: chloroform, +0·14; acetone, +0·40; methyl alcohol, +0·48. Phenetole: chloroform, +0·39; acetone, +0·40; methyl alcohol, +0·71. Quinol dimethyl ether: chloroform, +0·35; methyl alcohol, +1·15. Nitrobenzene: chloroform, +0·13; acetone, +0·99; methyl alcohol, +0·74. *p*-Nitroanisole: chloroform, +2·68; acetone, +3·27; methyl alcohol, +3·60. *p*-Nitrophenetole: chloroform, +2·99; acetone, +3·61; methyl alcohol, +3·93. *p*-Nitrophenol: *iso*butyl butyrate, +2·79; acetone, +3·70; methyl alcohol, +3·84. *o*-Nitrophenol: chloroform, +1·89; acetone, +2·62; methyl alcohol, +2·69. Nitroquinol dimethyl ether: chloroform, +1·45; methyl alcohol, +2·42.

These results show that, contrary to Kauffmann's statement, the more strongly dissociating the solvent the more the nature of the solute is changed on solution. G. Y.

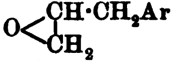
Dibromides of Allyl Phenolic Ethers. Formation of *cyclo*-Propanols. MARC TIFFENEAU and DAUFRESNE (*Compt. rend.*, 1907, **144**, 924—926).—In the dibromides of the allyl phenolic ethers, the bromine atom nearer the benzene nucleus is easily replaced (compare Pond, Abstr., 1902, i, 449; 1903, i, 417; Hell, 1904, i, 385; Hœring, 1904, i, 577; 1905, i, 592, 903). Thus, when heated with alcoholic potassium acetate solution, acetylbromohydrins are formed,

$$Ar\cdot CH_2\cdot CHBr\cdot CH_2Br \longrightarrow Ar\cdot CH_2\cdot CH(OAc)\cdot CH_2Br.$$

The latter when heated with alcoholic potash are transformed into *cyclo*propanols, $Ar\cdot CH_2\cdot CH(OAc)\cdot CH_2Br \longrightarrow$  $CH_2<\begin{array}{l}CH\cdot Ar\\ CH\cdot OH\end{array}$, a ring-formation analogous to those observed by Henry (*Bull. Acad. roy. Belg.*, 1899, [iii], **37**, 17) and Lipp (Abstr., 1889, 843). The *cyclo*propanols so obtained are isomeric with the ethylene oxides,


$$O<\begin{array}{l}CHAr\\ CHMe\end{array}$$

or


$$O<\begin{array}{l}CH\cdot CH_2Ar\\ CH_2\end{array}$$

(Idzkowska and Wagner, Abstr., 1899, i, 489), but are distinguished from them by their conversion into hydratropaldehydes,

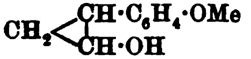
$$Ar\cdot CHMe\cdot CHO,$$

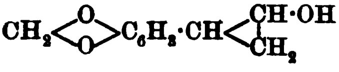
whilst the oxides of the first formula are transformed into aryl acetones, $Ar\cdot CH_2\cdot COMe$ (Hoering), and those of the second into hydrocinnamaldehydes, $Ar\cdot CH_2\cdot CH_2\cdot CHO$ (Fourneau and Tiffeneau, Abstr., 1905, i, 591).

Estragole dibromide, obtained by direct bromination, has b. p. 188—192°/18 mm. (decomp.), D^{17} 1·639; when heated with alcoholic potassium acetate it gives *p-anisylacetylbromohydrin*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CH(OAc)\cdot CH_2Br,$$

b. p. 160°/13 mm. (decomp.), D^0 1·249, which on heating with alcoholic potash is transformed into *anisyl*cyclo*propanol* in the form of slender needles, m. p. 79°. The latter is formed directly from the dibromide by boiling with aqueous potassium carbonate solution. When *anisyl*cyclo*propanol* is boiled under ordinary pressure (b. p. 250—260°), it undergoes isomeric change into *p*-methoxyhydratropaldehyde already described. The propanol gives an *acetate*, b. p. 164—165°/13 mm., D^0 1·123. Safrole dibromide similarly gives an alcohol, $C_{10}H_{10}O_3$, b. p. 170—178°/15 mm., D^0 1·286, which must be 3 : 4-*methylenedioxyphenyl*cyclo*propanol*, since it changes into the isomeric *methylenedioxyhydratropaldehyde*, which gives a *semicarbazone*, m. p. 158°, and an *oxime*, m. p. 71°. This propanol gives an *acetate* having D^0 1·255. E. H.

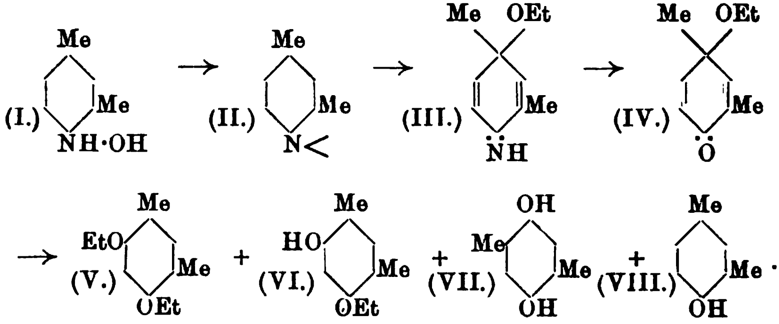

$$CH_2<\begin{array}{l}CH\cdot C_6H_4\cdot OMe\\ CH\cdot OH\end{array}$$


$$CH_2<\begin{array}{l}O\\ O\end{array}>C_6H_3\cdot CH<\begin{array}{l}CH\cdot OH\\ CH_2\end{array}$$

Iodo-derivatives of the Methyl Ethers of Catechol. EUGÈNE TASSILLY and J. LEROIDE (*Compt. rend.*, 1907, **144**, 757—759).—When guaiacyl acetate, prepared by the action of acetic anhydride on guaiacol, is treated with iodine and mercuric oxide in the presence of carbon tetrachloride and a dehydrating agent (preferably acetic anhydride), *iodoguaiacyl acetate*, $OMe\cdot C_6H_3I\cdot OAc$, m. p. 74°, is obtained. Similarly, guaiacyl benzoate gives *iodoguaiacyl benzoate*, $OMe\cdot C_6H_3I\cdot OBz$, m. p. 80—81°. Either of these compounds when treated with potash gives an alkali salt, from the solution of which, acids precipitate *iodoguaiacol*, $OH\cdot C_6H_3I\cdot OMe$, in small, brilliant, colourless spangles, m. p. 87—88°. This is identical with the iodoguaiacol prepared from Cousin's nitroguaiacol (*J. Pharm.*, [vi], 9, 276) by reduction and diazotisation, and hence has the constitution $OH : OMe : I = 1 : 2 : 4$. The latter is confirmed by the production on methylation of an iodoveratrole (m. p. 34—35°) identical with that obtained from veratrylamine by the diazo-reaction. Nitric and sulphuric acids set free iodine from iodoguaiacol, forming nitroguaiacol and guaiacolsulphonic acids respectively. Attempts to demethylate iodoguaiacol resulted in the removal of iodine as well as the methyl group.

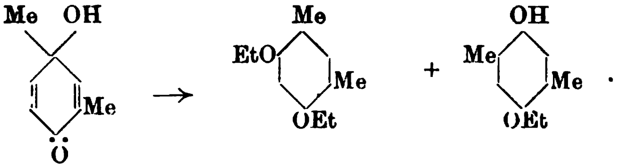
The substance gives a *sodium* salt which forms silky needles decomposed by the carbon dioxide of the atmosphere. E. H.

Transformations with Arylhydroxylamine and Quinol Derivatives. EUGEN BAMBERGER (*Ber.*, 1907, 40, 1893—1906. Compare Abstr., 1903, i, 83).—A résumé of results obtained in an extended study of arylhydroxylamines and quinols. Xylylhydroxylamine, when warmed with a mixture of concentrated sulphuric acid (1 vol.) and ethyl alcohol (30 vols.), is transformed successively into iminoxyloquinol ether (III), xyloquinol ether (IV), and a mixture of xylorcinol diethyl ether (V) and xylorcinol monoethyl ether (VI); at the same time, small amounts of xylohydroquinone and *as*-xylenol are formed, thus:

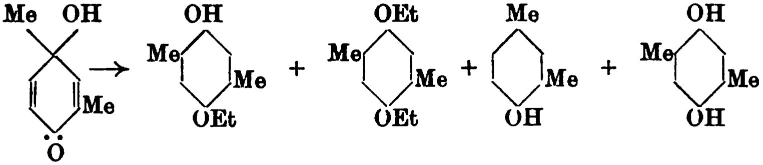


In order to obtain iminoquinol ethers, which decompose with great ease to form ammonia and quinol ethers, water must be rigidly excluded.

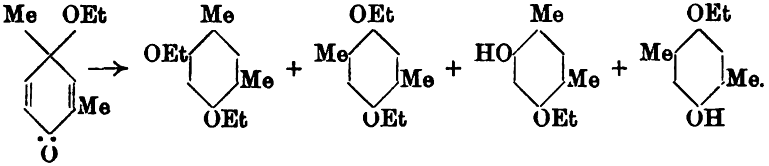
Xyloquinol is transformed by the action of a mixture of alcohol (30 vols.) and sulphuric acid (1 vol.) into a mixture of *m*-xylorcinol diethyl ether and *p*-xylohydroquinone monoethyl ether:



Xyloquinol is transformed by the action of a mixture of alcohol (2 vols.) and sulphuric acid (1 vol.) into a mixture of xylohydroquinone monoethyl ether, *as*-xylenol, and xylohydroquinone, together with a little xylohydroquinone diethyl ether :

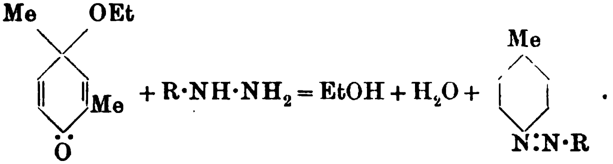


When xyloquinol ether is warmed with a mixture of concentrated sulphuric acid (1 vol.) and ethyl alcohol (30 vols.), the main product is *m*-xylorcinol diethyl ether ; *p*-xylohydroquinone diethyl ether is also formed together with a little xylorcinol monoethyl ether and possibly traces of *p*-xylohydroquinone monoethyl ether :



The rest of the paper, which deals with the theoretical aspect of the subject, does not lend itself to adequate abstraction. A. McK.

Action of Ethyl- and Methyl-alcoholic Sulphuric Acid on *as-m*-Xylylhydroxylamine. I. Xyloquinol Ether. Eugen Bamberger (*Ber.*, 1907, **40**, 1906—1917. Compare preceding abstract).—The main product of the action of a mixture of ethyl alcohol and sulphuric acid on *as-m*-xylylhydroxylamine is a neutral oil, $C_{10}H_{14}O_2$, which is shown to be the ethyl ether of 1 : 3-dimethylquinol, since it combines with *p*-nitrophenylhydrazine or with semicarbazide with the elimination of ethyl alcohol and the formation of an azo-compound :



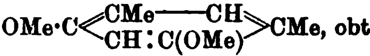
The formation of a quinol ether is characteristic of para-alkylated arylhydroxylamines; if the substitution of the alkyl group in the arylhydroxylamine takes place elsewhere than in the para-position, the action of alcoholic sulphuric acid on the resulting compound is to form phenetidine.

1 : 3-*Xyloquinol ethyl ether* (IV, preceding abstract) is an almost colourless oil, b. p. 94—94·5°/12 mm. It is volatile with steam and has an odour reminiscent of that of menthol. It has D^{17} 0·9957. When shaken with semicarbazide hydrochloride, it forms *p*-xylylazocarboxylamide, orange-red needles, m. p. 135—136°, whilst with *p*-nitrophenylhydrazine hydrochloride, it forms *p*-nitrobenzeneazo-xylene, m. p. 128·5—129·5°.

m-*Xylorcinol diethyl ether* (see preceding abstract, V), obtained together with the preceding compound, has m. p. 75°. Azoxyxylene and azoxylene were also identified as products of the action.

m-*Xylorcinol monoethyl ether* (preceding abstract, VI) separates from light petroleum in glistening leaflets and, when reduced by hydriodic acid, is converted into *m*-xylorcinol. *as-m-*Xylenol was identified by the formation of a mononitro-derivative.

The following products were obtained from 100 grams of *as-m-*xylylhydroxylamine: (1) 30 grams of 1 : 3-dimethylquinol ethyl ether, (2) 7 grams of *m*-xylorcinol diethyl ether, (3) about 0·15 gram of *m*-xylorcinol monoethyl ether, (4) about 0 2 gram of *as-m*-xylenol, (5) about 5 grams of azoxyxylene, (6) about 0·1 gram of azo-xylene, (7) a very little *p*-xylohydroquinone, (8) 2·7 grams of bases, (9) much resin and ammonia, possibly also an appreciable amount of *p*-xylohydroquinone diethyl ether, and a little of the corresponding monoethyl ether.

m-*Xylorcinol dimethyl ether*, 
$OMe\cdot C{<}\begin{array}{l}CMe{-}{-}{-}CH\\CH:C(OMe)\end{array}{>}CMe$, obtained by heating *as-m-*xylylhydroxylamine (5 grams) with a mixture of methyl alcohol (70 c.c.) and concentrated sulphuric acid (2·5 grams) for three to four hours at 100°, has m. p. 76°

1 : 3-Xyloquinol ethyl ether may also be obtained from xyloquinol by ethylating it with ethyl iodide and sodium ethoxide.

A. McK.

Action of Ethyl- and Methyl-alcoholic Sulphuric Acid on *as-m*-Xylylhydroxylamine. II. Imino-xyloquinol Ethers.

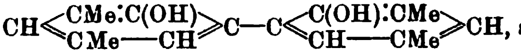
EUGEN BAMBERGER (*Ber.*, 1907, 40, 1918—1932. Compare preceding abstracts).—The formation of iminoxyloquinol ether as an intermediate product in the conversion of *as-m*-xylylhydroxylamine into 2 : 4-dimethylquinol ether occurs when a mixture of concentrated and fuming sulphuric acids is used and when the action is interrupted at the proper time. The following products are also obtained: (1) xyloquinol ether, (2) xyloquinol, (3) *p*-xylohydroquinone diethyl ether, (4) *as-m*-xylenol, (5) *as-m*-azoxyxylene, (6) *as-m*-dixylenol, (7) *p*-xyloquinone, (8) *as-m*-xylidine, (9) resin, ammonia, and another substance.

4-*Imino*-1 : 3-*dimethylquinol* 2-*ethyl ether* (III, p. 516) is an almost colourless oil, b. p. 98—98·5°/11 mm., soluble in mineral acids, from the solutions in which it is precipitated by alkalis. It is readily hydrolysed by water, slowly at the ordinary temperature and quickly at 100°, thus: $OEt{:}C_6H_3Me_2{:}NH + H_2O = OEt{\cdot}C_6H_3Me_2{:}O + NH_3$, imino-xyloquinol ether being formed.

4-*Chloroimino*-1 : 3-*dimethylquinol ethyl ether*, $OEt{\cdot}C_6H_3Me_2{:}NCl$, obtained by the addition of the imino-ether to an aqueous solution of bleaching powder, forms glistening needles or prisms, m. p. 31·5°, has an odour of bleaching powder, is volatile with steam, and liberates iodine from potassium iodide.

When the imino-ether is dissolved in dilute sulphuric acid and sodium nitrite added, a product is obtained which gives a marked Liebermann reaction.

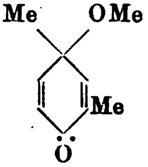
The presence of the imino-group in the imino-ether is also shown by the formation of a *benzoyl* derivative, $OEt{\cdot}C_6H_3Me_2{:}NBz$, which separates from alcohol or benzene in silky, colourless needles, m. p. 79—80°.



$$CH\begin{matrix}\diagup\!\!\!^{CMe{:}C(OH)}\diagdown \\ \diagdown_{CMe\text{——}CH}\diagup\end{matrix}C\text{—}C\begin{matrix}\diagup\!\!\!^{C(OH){:}CMe}\diagdown \\ \diagdown_{CH\text{——}CMe}\diagup\end{matrix}CH$$

as-m-*Dixylenol*, $CH{<}^{CMe{:}C(OH)}_{CMe\text{——}CH}{>}C\text{—}C{<}^{C(OH){:}CMe}_{CH\text{——}CMe}{>}CH$, separates from dilute alcohol in needles, m. p. 137·5—138° (compare Brun, *Inaug. Diss. Zürich*, 1902).

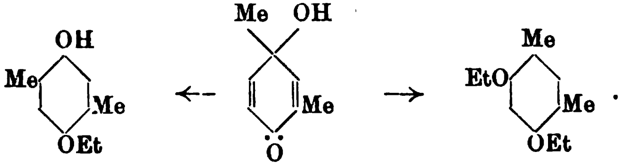
The action of methyl alcohol on *as-m*-xylylhydroxylamine in the presence of concentrated sulphuric acid is analogous to that of ethyl alcohol.



4-*Imino*-1 : 3-*dimethylquinol* 2-*methyl ether*, $NH{:}C_6H_3Me_2{\cdot}OMe$, is a yellow oil, b. p. 94—95°/13 mm. The *chloroimide* forms glistening prisms, m. p. 62·5—63·5°. The imino-ether is readily hydrolysed by water with the formation of 1 : 3-*dimethylquinol methyl ether* (annexed formula), which forms colourless, glistening prisms, m. p. 40—45°. When its aqueous solution is shaken with *p*-nitrophenylhydrazine hydrochloride, *p*-nitrobenzeneazoxylene, m. p. 128·5—129·5°, is formed.

A. McK.

Action of Aliphatic Alcohols on 1 : 3-Dimethylquinol in the Presence of Concentrated Sulphuric Acid. EUGEN BAMBERGER and JOHANNES FREI (*Ber.*, 1907, 40, 1932—1949. Compare preceding abstracts).—When 1 : 3-dimethylquinol is acted on by ethyl alcohol in the presence of a little sulphuric acid, it is converted into a mixture of the acid ether of *p*-xylohydroquinone and the normal ether of *m*-xylorcinol, the proportions of which vary according to the temperature at which the action is conducted:



The constitution of these ethers was determined. The acid ether was hydrolysed by hydriodic acid to *p*-xylohydroquinone; it is also formed by ethylating the latter. The normal ether was hydrolysed to form *m*-xylorcinol; it is re-formed when the latter is ethylated.

The formation of these two ethers by the action of ethyl alcohol is a general one. Methyl, *n*-propyl, and *n*-butyl alcohols interact with xyloquinol in an analogous manner.

p-*Xylohydroquinone monoethyl ether* forms silky needles, m. p. 80·5—81·5°. Evidence for its constitution is also quoted in its formation from *p*-dimethyl-*p*-phenetidine, where the amino-group is replaced by the hydroxyl group in the usual manner.

m-*Xylorcinol diethyl ether* separates from alcohol in glistening needles, m. p. 75° and b. p. 132°/15 mm.

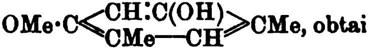
m-*Xylorcinol dimethyl ether*, $C_{10}H_{14}O_2$, forms colourless needles, glistening leaflets or plates, m. p. 76°. It is converted by hydriodic acid into methyl iodide and *m*-xylorcinol, and is re-formed by methylating the latter.

p-*Xylohydroquinone monomethyl ether*, $C_9H_{12}O_2$, separates from light petroleum in silky needles, m. p. 90°. Hydriodic acid converts it into *p*-xylohydroquinone. It may also be formed from dimethyl *p*-anisidine.

m-*Xylorcinol dipropyl ether*, $C_{14}H_{22}O_2$, separates from alcohol in silky needles, m. p. 33·5°. Hydriodic acid hydrolyses it to *m*-xylorcinol.

p-*Xylohydroquinone monopropyl ether*, $C_{11}H_{16}O_2$, separates from light petroleum in silky needles, m. p. 75°.

p-*Xylohydroquinone mono*-n-*butyl ether* has m. p. 40—45°. m-*Xylorcinol di*-n-*butyl ether*, $C_{16}H_{26}O_2$, separates from alcohol in leaflets, m. p. 42°. It is hydrolysed by hydriodic acid to *m*-xylorcinol.

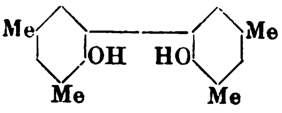
m-*Xylorcinol monomethyl ether*,  $\mathrm{OMe\cdot C}\left\langle\begin{matrix}\mathrm{CH{:}C(OH)}\\ \mathrm{CMe{-}CH}\end{matrix}\right\rangle\mathrm{CMe}$, obtained by the action of sodium methoxide and methyl iodide on *m*-xylorcinol, separates from light petroleum in silky, felted needles, m. p. 78°.

A. McK.

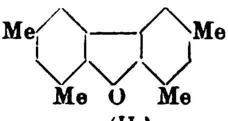
Action of Alcoholic Sulphuric Acid on 1 : 3-Dimethylquinol.

EUGEN BAMBERGER and JOSEF BRUN (*Ber.*, 1907, 40, 1949—1955. Compare preceding abstracts).—Whilst 2 : 4-xyloquinol is converted by a little strong sulphuric acid at the ordinary temperature, mainly into *m*-xylorcinol diethyl ether, but in small amount into *p*-xylohydroquinone monoethyl ether together with traces of *p*-xylohydroquinone and *as*-*m*-xylenol, the action of more acid causes the formation of about the same amount of *p*-xylohydroquinone monoethyl ether, but no *m*-xylorcinol diethyl ether is obtained; the amount of *as*-*m*-xylenol and of *p*-xylohydrochinone formed increases, however, and other substances are obtained, namely, *p*-xylohydroquinone diethyl ether, an amorphous acid, probably $C_{11}H_{12}O_2$, and dixylenol (I).

That the two benzene nuclei are in the ortho-positions to the hydroxy-groups is shown by the behaviour of dixylenol when heated, when a substance, $C_{16}H_{16}O$, probably a tetramethylated dibenzofuran (II), is obtained. p-*Xylohydroquinone monoethyl ether* has m. p. 80·5—81·5°. *Dixylenol* separates from light



(I.)



(II.)

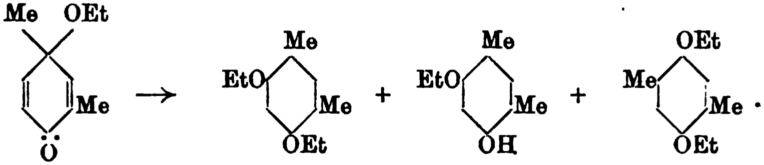
petroleum in rhombic plates or glistening needles, m. p. 137·5—138°. It gives an olive-green coloration with ferric chloride.

Tetramethyldibenzofuran separates from 90% alcohol in nacreous leaflets, m. p. 90—90·5°, and is insoluble in alkali.

p-Xylohydroquinone diethyl ether was identified by its odour of peppermint, its m. p. 106—107°, and by its conversion by hydriodic acid into *p*-xylohydroquinone.

A *compound*, $C_{16}H_{16}O_4$, of a quinone nature was also obtained, m. p. 297—298°.
A. McK.

Transformations of 2 : 4-Dimethylquinol Ethyl Ether. Eugen Bamberger (*Ber.*, 1907, **40**, 1956—1958. Compare preceding abstracts).—2 : 4-Dimethylquinol ethyl ether, when left in contact with alcoholic sulphuric acid, is transformed into a mixture of *m*-xylorcinol diethyl ether, *m*-xylorcinol monoethyl ether, and *p*-xylohydroquinone diethyl ether, thus,



In this mixture, *m*-xylorcinol diethyl ether predominates.
A. McK.

Unsaponifiable Matter in Chrysalidene Oil. Julius Lewkowitsch (*Zeitsch. Nahr. Genussm.*, 1907, **13**, 552).—Chrysalidene oil, the first fatty oil derived from insects (*ibid.*, 1906, **12**, 659), was examined to see if, like all other fats and oils of animal origin, it contained cholesterol. The unsaponifiable matter from the oil, when heated with acetic anhydride, is separated into two constituents, cholesterol and a hydrocarbon, m. p. 54—62°
T. A. H.

Phytosterol of the Soy Bean. Timothée Klobb and Armand Bloch (*Bull. Soc. chim.*, 1907, [iv], 1, 422—428).—The phytosterol obtained by Meissl and Böcker (Abstr., 1883, 1024) has been prepared from yellow, black, and pale green varieties of Soy beans, *Glycine hispida*. It has the composition $C_{26}H_{44}O,H_2O$, m. p. 136°, $[\alpha]_D$ $-32·03°$ in chloroform, or $-28·69°$ in ether, and crystallises in warm alcohol in lamellæ. It gives the usual colour reactions of the phytosterols. The *benzoyl* derivative, m. p. 141—142°, $[\alpha]_D$ $-13·77°$ in chloroform, crystallises from boiling alcohol in rectangular lamellæ. The *acetate*, m. p. 130—131° when freshly prepared, or 125—126° on keeping, forms silky, hexagonal lamellæ from alcohol. Comparison of this phytosterol with the similar substances already known indicates that it is probably new, and the author proposes for it the name *sojasterol*.
T. A. H.

Stereoisomeric γ-*p*-Methoxyphenyl-βγ-propyleneglycols [γ-*p*-Methoxyphenylpropane-βγ-diols]. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 477—484).—The author has repeated the work of Varenne and Godefroy (Abstr., 1905, i, 282) on the action of alcoholic potassium hydroxide on dibromoanethole, his results being quite different from those obtained by these authors. He has also succeeded in separating the two stereoisomeric glycols formed in the oxidation of anethole by mercuric acetate (Abstr., 1902, i, 808), neither of these glycols being identical with the glycol described by Varenne and Godefroy (*loc. cit.*).

[With VINCENZO PAOLINI and G. DE CONNO.]—The action of alcoholic potassium hydroxide solutions of various concentrations on dibromoanethole, prepared according to Hell and Günthert's directions (Abstr., 1896, i, 20), does not yield γ-*p*-methoxyphenylpropane-βγ-diol (Varenne and Godefroy, *loc. cit.*), but always gives anisyl ethyl ketone (Wallach and Pond, Abstr., 1896, i, 94).

The γ-*p*-methoxyphenylpropane-βγ-diol, m. p. 98°, obtained by the action of mercuric acetate on anethole (Balbiani, Paolini, and Nardacci, Abstr., 1902 i, 808), consists of a mixture of two stereoisomerides: (1) the β-modification, $C_{10}H_{14}O_3$, which crystallises from 95% alcohol in aggregates of microscopic needles or from water in shining, superposed laminæ, m. p. 114—115°, and (2) the α-form, which crystallises from water with $3H_2O$ in aggregates of shining laminæ, m. p. 30—31° or, for the anhydrous compound, 62—63°; when heated, the α-modification is partially transformed into the β-form. The α-compound yields a *diacetyl* derivative, $OMe\cdot C_6H_4\cdot C_3H_5(OAc)_2$, which is a viscous liquid, b. p. 203°/20 mm., dissolving in alcohol, and undergoing transformation into a mixture of the α- and β-glycols on hydrolysis with sodium ethoxide. T. H. P.

αα-Diphenylglycerol. CARL PAAL and KURT ZAHN (*Ber.*, 1907, 40, 1819—1821. Compare Abstr., 1906, i, 400, 802).—The preparation of tri-, tetra-, and penta-hydric alcohols has been undertaken in extension of an investigation of diaryl substituted hexoses (*loc. cit.*), and that of *r*-αα-diphenylglycerol is described now.

r-αα-Diphenyglycerol (*αα-diphenylpropan-αβγ-triol*),

$$OH\cdot CPh_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

formed by the action of magnesium phenyl bromide on methyl *r*-glycerate, in a 42% yield, crystallises in colourless plates, m. p. 157—158°, and distils in small amounts almost unchanged. G. Y.

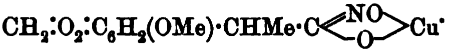
Myristicin. ENRICO RIMINI and F. OLIVARI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 663—665).—When myristicin and *iso*myristicin are treated in alcoholic solution with iodine and yellow mercuric oxide they yield the corresponding iodohydroxy-compounds. In the case of *iso*myristicin, however, the use of an excess of mercuric oxide determines the formation of a considerable quantity of an acetal, just as was found by Bougault with *iso*safrole (Abstr., 1902, i, 452). These results confirm the conclusion previously arrived at (compare Rimini, Abstr., 1905, i, 198) that myristicin contains an allyl and *iso*myristicin a propenyl side-chain.

The iodohydroxy-derivative of *myristicin*, $CH_2{:}O_2{:}C_6H_2(OMe)\cdot CH_2\cdot CHI\cdot CH_2\cdot OH$ or $CH_2{:}O_2{:}C_6H_2(OMe)\cdot CH_2\cdot CH(OH)\cdot CH_2I$, prepared by the action of iodine and yellow mercuric oxide on an alcoholic solution of myristicin, is a dense, colourless, highly refractive oil which decomposes on heating.

The corresponding derivative of iso*myristicin*, $CH_2{:}O_2{:}C_6H_2(OMe)\cdot CHI\cdot CHMe\cdot OH$ or $CH_2{:}O_2{:}C_6H_2(OMe)\cdot CH(OH)\cdot CHMeI$, prepared by the action of iodine (4 mols.) and yellow mercuric oxide (1 mol.) on *iso*myristicin (2 mols.), is obtained as an oily liquid. If the proportion of mercuric oxide used is doubled, this reaction yields *dioxymethylenemethoxyhydratropaldehyde*,

$$CH_2{:}O_2{:}C_6H_2(OMe)\cdot CHMe\cdot CHO,$$

which is an oily liquid, b. p. 288—290°; its *semicarbazone*, $C_{12}H_{15}O_4N_3$, crystallises from alcohol in white, mamillary masses, m. p. 140°; treatment of the aldehyde with benzenesulphydroxylaminic acid gives a hydroxamic acid, which yields an intense reddish-violet coloration with ferric chloride and forms an insoluble bottle-green *copper* compound,



$CH_2{:}O_2{:}C_6H_2(OMe)\cdot CHMe\cdot C{<}\genfrac{}{}{0pt}{}{NO}{O}{>}Cu\cdot$

T. H. P.

Constitution of Myristicin and its Derivatives. Oscar Richter

(*Ber. Deut. pharm. Ges.*, 1907, 17, 152—161).—An account is given of the views of Semmler (Abstr., 1890, 1150; 1892, 311) and of Thoms (Abstr., 1904, i, 47) as to the constitution of myristicin and its derivatives. The product obtained on reduction of *iso*myristicin by means of sodium and alcohol was considered by Thoms (*loc. cit.*) to be 5-methoxy-3-propylphenol, as the corresponding dimethoxypropylbenzene was found to be isomeric with dihydromethyleugenol. This is confirmed now by oxidation of the dimethoxypropylbenzene with potassium permanganate in alkaline solution, the product being identical with dimethyl-*a*-resorcylic acid (3 : 5-dimethoxybenzoic acid), m. p. 182° (175—176°: Tiemann and Streng, Abstr., 1882, 51), obtained by oxidation of orcinol dimethyl ether. A mixture of the oxidation product of the dimethoxypropylbenzene from *iso*myristicin with veratric acid, m. p. 181°, melted at 36°.

The action of bromine on 3 : 5-dimethoxypropylbenzene in glacial acetic acid at 0° leads to the formation of a *dibromo*-derivative, which on nitration yields a mixture of *bromonitro*- and *dinitro*-3-*methoxy*-5-*propylbenzenes*.

Dihydromyristicin forms a *dibromo*-derivative, from which the bromine can be removed by reduction with sodium and alcohol. Attempts to remove the bromine from the side-chain of dibromomyristicin dibromide led to results similar to those obtained by Höring with tribromo*iso*safrole dibromide (this vol., i, 411).

G. Y.

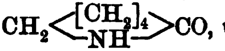
Synthesis of Amino-Acids from Cyclic Imines. JULIUS VON BRAUN (*Ber.*, 1907, **40**, 1834—1846. Compare Abstr., 1906, i, 576; this vol., i, 151).—Cyclic imine bases are converted by Schotten's method (Abstr., 1883, 813; 1885, 176; 1886, 1104; Bunzel, Abstr., 1889, 904; Bamberger and Dieckmann, Abstr., 1893, i, 528) into amino-acids containing the same or a smaller number of carbon atoms in the nucleus. In this paper a method is described which leads to the formation of amino-acids having a number of carbon atoms in their molecules greater than is contained in the nuclei of the cyclic imine bases from which they are obtained. The new method consists in the conversion of the acylimines, $R\dot{:}N\cdot COR'$, by the action of phosphorus pentachloride into the chloro-amides, $COR'\cdot NH\cdot R\cdot Cl$, which are condensed with potassium cyanide or ethyl malonate, forming the nitriles, $COR'\cdot NH\cdot R\cdot CN$, or substituted malonic esters,

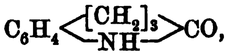
$$COR'\cdot NH\cdot R\cdot CH(CO_2Et)_2;$$

these on hydrolysis yield the amino-acids, $NH_2\cdot R\cdot CO_2H$ and

$$NH_2\cdot R\cdot CH_2\cdot CO_2H.$$

The series of reactions, which take place readily, leads to the formation of ε- and ζ-amino-acids from hexa-atomic, or of δ- and ε-amino-acids from penta-atomic, cyclic imines. The formation of ε-leucine and ζ-amino-*n*-heptoic acid from piperidine and of *o*-aminophenylbutyric and *o*-aminophenylvaleric acids from tetrahydroquinoline is described.

Whilst on loss of water, ε-leucine forms a small amount of the anhydride,  $CH_2<\genfrac{}{}{0pt}{}{[CH_2]_4}{NH}>CO$, together with much of the polymeric anhydride, $(\cdot CO\cdot[CH_2]_5\cdot NH\cdot)_x$, ζ-amino-*n*-heptoic acid forms only the polymeric lactam, $(\cdot NH\cdot[CH_2]_6\cdot CO\cdot)_x$ (compare Gabriel and Maass, Abstr., 1889, i, 595; Manasse, Abstr., 1902, i, 351).

o-*Aminophenylbutyric* acid can be isolated only in the form of its salts with acids or bases, since on liberation it immediately loses water, yielding the *lactam*,  $C_6H_4<\genfrac{}{}{0pt}{}{[CH_2]_3}{NH}>CO$, termed *homohydrocarbostyril*, which is hydrolysed by concentrated acids or alkalis (compare Fischer and Kuzel, Abstr., 1883, 1132). The conclusion is drawn that hepta-atomic rings are more capable of existence in the aromatic than in the aliphatic series.

*Benzoyl-ε-amino-*n*-hexonitrile*, $NHBz\cdot[CH_2]_5\cdot CN$, m. p. 95°, is hydrolysed by concentrated hydrochloric acid under pressure at 160—170°. *Benzenesulphonyl-ε-leucine*, $SO_2Ph\cdot NH\cdot[CH_2]_5\cdot CO_2H$, crystallises in long needles, sinters at 120°, m. p. 122°.

*Benzenesulphonyl-ζ-amino-*n*-heptoic acid*, $SO_2Ph\cdot NH\cdot[CH_2]_6\cdot CO_2H$, m. p. 80°, crystallises from hot water.

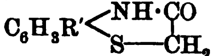
*Benzoyl-*o*-γ-iodo-*n*-propylanilide*, $NHBz\cdot C_6H_4\cdot C_3H_6I$, formed by the action of sodium iodide on the chloro-compound in alcoholic solution, is obtained in white crystals, m. p. 112—113°. *Benzoyl-o-aminophenylvaleric acid*, $NHBz\cdot C_6H_4\cdot[CH_2]_4\cdot CO_2H$, forms white crystals, m. p. 127°.

Benzoyl-o-aminophenylbutyronitrile, $NHBz\cdot C_6H_4\cdot[CH_2]_3\cdot CN$, crystallises in white needles, m. p. 128°, and is hydrolysed by fuming hydrochloric acid under pressure at 125°. *Homohydrocarbostyril*, formed by heating the hydrochloride of γ-*o*-aminophenylbutyric acid or on liberation of the butyric acid, crystallises in yellow needles, m. p. 139—140°. The *hydrochloride*, white needles, m. p. 201°, and *platinichloride*, m. p. 208°, of γ-*o*-aminophenylbutyric acid are described. γ-o-*Benzoylaminophenylbutyric acid*,

$$NHBz\cdot C_6H_4\cdot[CH_2]_3\cdot CO_2H,$$

forms white crystals, m. p. 156°. *Ethyl γ-o-aminophenylbutyric acid*, $NH_2\cdot C_6H_4\cdot C_3H_6\cdot CO_2Et$, is obtained as a colourless, viscid oil, b. p. 191°/10 mm., and forms a syrupy *hydrochloride*, a readily soluble *platinichloride*, and a *benzoyl* derivative, $NHBz\cdot C_6H_4\cdot C_3H_6\cdot CO_2Et$, crystallising in white leaflets, m. p. 97°. G. Y.

Arylthioglycollic [Arylthiolacetic] Acids. Paul Friedländer and A. Chwala [and, in part, Z. Slubek] (*Monatsh*, 1907, **28**, 247—280. Compare Friedländer and Mauthner, Abstr., 1905, i, 102; Friedländer, Abstr., 1906, i, 378; this vol., i, 334).—Thiolacetic acid (Holmberg, Abstr., 1905, i, 323; Klason and Carlson, Abstr., 1906, i, 232) is obtained in almost quantitative yields by adding a concentrated solution of sodium chloroacetate to a hot concentrated solution of sodium disulphide prepared by addition of flowers of sulphur to fused commercial sodium sulphide, and reduction of the resulting dithioglycollic acid with zinc dust and dilute sulphuric acid. In aqueous solution, thiolacetic acid reacts quantitatively with diazo-salts, forming stable arylazothiolacetic acids, $N_2R\cdot S\cdot CH_2\cdot CO_2H$, which detonate feebly when heated in the dry state, and when heated with water or indifferent solvents lose nitrogen and form arylthiolacetic acids, $SR\cdot CH_2\cdot CO_2H$, the yields being almost quantitative, especially if the aryl nucleus contains negative groups such as hydroxyl or carboxyl. Nitro- and dinitro-phenylthiolacetic acids are formed by the action of *o*- and *p*-chloronitrobenzene and *l*-chloro-2:4-dinitrobenzene on thiolacetic acid in presence of potassium hydroxide; on reduction with tin and hydrochloric acid the *o*-nitrophenylthiolacetic acids yield 3-keto-3:4-dihydro-1:4-benzothiazines,



$$C_6H_3R'<\begin{matrix}NH\cdot CO\\ |\quad\;\; |\\ S—CH_2\end{matrix}$$

(compare Hofmann, Abstr., 1880, 389).

Diazobenzene chloride reacts with thioacetic acid in aqueous solution forming *diazobenzene thioacetate*, which is obtained as an unstable, colourless oil. Thioacetates of substituted diazobenzenes are mostly crystalline; the diazo-thioacetates derived from *p*-nitro- and *p*-bromoaniline, which are slightly more stable, are described.

p-*Nitrodiazobenzene thioacetate*, $NO_2\cdot C_6H_4\cdot N_2\cdot S\cdot COMe$, crystallises from a mixture of chloroform and light petroleum in yellow needles, detonates when heated, decomposes slowly at the ordinary temperature, more quickly in solution, and does not couple with β-naphthol in alkaline solution. When heated in alcoholic solution, it yields nitrobenzene, sulphur, and gives an odour of aldehyde; the action of iodine in alcoholic solution leads to the formation of nitro- and *p*-iodonitrobenzene. When heated with anhydrous thioacetic acid, the nitrodiazothioacetate yields as-*diacetyl*-p-*nitrophenylhydrazide* and small amounts of *p*-nitroacetanilide; if the thioacetic acid is evaporated, triacetyl-*p*-nitrophenylhydrazide, or if moisture is present, *s*-acetyl-*p*-nitrophenylhydrazide, is formed.

as-*Diacetyl*-p-*nitrophenylhydrazide*, $NO_2\cdot C_6H_4\cdot NH\cdot NAc_2$, crystallises in yellow needles, m. p. 181·5°, is soluble in aqueous sodium hydroxide or carbonate, less so in ammonia, is reprecipitated unchanged by acids, yields *p*-phenylenediamine on reduction with tin and hydrochloric acid, and when boiled with concentrated hydrochloric acid forms *p*-nitrophenylhydrazine hydrochloride.

p-*Bromodiazobenzene thioacetate*, $C_6H_4Br\cdot N_2\cdot S\cdot COMe$, crystallises in yellow needles, closely resembles the *p*-nitro-compound, and yields *p*-bromoiodobenzene when treated with alcoholic iodine or *s*-acetyl-*p*-bromophenylhydrazine with thioacetic acid.

p-*Tolylazothiolacetic acid*, $C_6H_4Me\cdot N_2\cdot S\cdot CH_2\cdot CO_2H$, crystallises in long, yellow needles, is decomposed by acids, and forms a stable *sodium* salt.

p-*Nitrophenylazothiolacetic acid*, $C_8H_7O_4NS$, crystallises in small, yellow needles; the *sodium* salt forms brownish-yellow leaflets.

p-*Carboxybenzeneazothiolacetic acid*, from *p*-aminobenzoic acid, crystallises in yellow needles, m. p. 153° (decomp.).

The *azothiolacetic acid* derived from β-naphthylamine forms a sparingly soluble *sodium* salt; the *acid* derived from α-aminoanthraquinone crystallises in colourless needles.

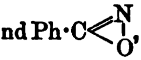
The following arylthiolacetic acids, $SR\cdot CH_2\cdot CO_2H$, are described; the temperatures are melting points.

$R = C_6H_4Me(o)$: flat needles, 108—109°, on oxidation with potassium permanganate in neutral solution yields o-*toluenesulphoneacetic acid*, $C_7H_7\cdot SO_2\cdot CH_2\cdot CO_2H$, colourless crystals, 107°; *silver* salt, $C_9H_9O_4SAg$, stable, colourless needles. $R = C_6H_4Me(p)$: colourless leaflets, 95°, when fused with sodium hydroxide yields *p*-thiocresol. $R = C_6H_4\cdot NO_2(o)$: light yellow needles, 162—164°, yields benzothiazole when heated with aqueous sodium hydroxide. $R = C_6H_4\cdot OH(o)$: brown oil, soluble in water, forms crystalline salts; the *barium* salt was analysed. $R = C_6H_4Cl(o)$: formed from *o*-aminophenylthiolacetic acid by Sandmeyer's reaction, colourless needles, 112°. $R = C_6H_4Cl(m)$: colourless needles, 81—82°. $R = C_6H_4Cl(p)$: colourless needles, 105°. $R = C_6H_4Br(p)$: yellow leaflets, 107°. $R = C_6H_4\cdot NO_2(p)$: from the corresponding azothiolacetic acid, or together with *pp'*-dichloroazoxybenzene from *p*-chloronitrobenzene, yellow needles, 156—158°; the *methyl* ester crystallises in stout yellow plates, 50—51°; the *ethyl* ester, yellow needles, 46—47°. $R = C_6H_4\cdot NH_2(p)$: by reduction of the *p*-nitro-acid, colourless needles, 196—197° (decomp.). $R = C_6H_3(NO_2)_2(op)$: yellow needles, 167—168°; the *methyl* ester, compact needles, 93—94°. $R = C_6H_4\cdot CO_2H(p)$: 267—269° (decomp.), forms soluble *alkali* salts; the *dimethyl* ester, $C_{11}H_{12}O_4S$, colourless needles, 63—64°; the *diethyl* ester, white needles, 98°.

The following 3-keto-3 : 4-dihydro-1 : 4-benzothiazines are described.

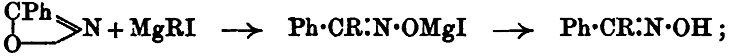
R' = 6-*amino*- : formed by reduction of 2 : 4-dinitrophenylthiolacetic acid, colourless needles, m. p. 222—224°, becomes brown when moist, forms soluble *salts*, and reduces platinum chloride in hydrochloric acid solution; the *acetyl* derivative, long needles, m. p. 257°. R' = 6-*chloro*- : formed from the 6-amino-compound by Sandmeyer's reaction, colourless needles, m. p. 205°, is converted by concentrated aqueous sodium hydroxide into 4-chloro-2-aminophenylthiolacetic acid. G. Y.

Nitrile Oxides. HEINRICH WIELAND (*Ber.*, 1907, 40, 1667—1676).—Benzonitrile oxide, prepared according to Werner's method from benzhydroxamic chloride and sodium hydroxide (Abstr., 1894, i, 585), is a solid, m. p. 15°. Its polymerisation into glyoxime peroxide takes place in one hour at the ordinary temperature; the change is hastened by alkali. This change has also been traced in an aqueous solution by determining the molecular weight at intervals by the freezing point method. The velocity of the reaction is dependent on the concentration and also on the nature of the solvent employed.

Of the two possible formulæ for this compound, $Ph\cdot C{\vdots}N{:}O$ and  $Ph\cdot C\!<\!\begin{smallmatrix}N\\|\\O\end{smallmatrix}$, the second is considered to be the more probable, for the following reasons. No additive compounds of the nature of amidoximes,

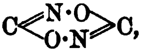
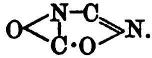
$$\cdot C{:}(NOH)\cdot NHR,$$

could be obtained, as ammonia, aniline, or phenylhydrazine are without action; the system $C{\vdots}N{:}O$ would be expected to be unsaturated. Bromine, iodine, hydrogen chloride, or phosphorus pentachloride do not react with the compound in the cold. It is quantitatively reduced by zinc dust to benzonitrile, and magnesium alkyl compounds give rise to ketoximes and ketones which can be most readily explained thus:



$$\begin{smallmatrix}CPh\\|\\O\end{smallmatrix}\!>\!N + MgRI \longrightarrow Ph\cdot CR{:}N\cdot OMgI \longrightarrow Ph\cdot CR{:}N\cdot OH;$$

magnesium methyl iodide gave acetophenone and acetophenoneoxime, magnesium ethyl iodide gave propiophenone and propiophenoneoxime and magnesium phenyl bromide, benzophenoneoxime, and an alkali soluble substance.

[With HUGO BAUER.]—Benzhydroxamic chloride decomposes spontaneously in a closed tube at 25—30° in the course of fourteen days into hydrogen chloride and dibenzenyloxoazoxime (Wieland and Bauer, Abstr., 1906, i, 412); no trace of glyoxime peroxide could be detected. This forms a good method for the preparation of the oxoazoxime. In contradistinction to the peroxide, it is basic, uniting with hydrogen chloride in the absence of water to form a *dihydrochloride*, $C_{14}H_{10}O_2N_2,2HCl$, m. p. 161° (decomp.); the hydrogen chloride is not lost in a vacuum. An oxonium salt is also obtained from hydroferricyanic acid. The interaction of phosphorus pentachloride and dibenzenyloxoazoxime, forming dibenzenyl-azoxime (*loc. cit.*), serves to show that the compound does not contain the six-membered ring,  $C\!<\!\begin{smallmatrix}N\cdot O\\O\cdot N\end{smallmatrix}\!>\!C$, but possesses the complex  $O\!<\!\begin{smallmatrix}N-C\\|\\C\cdot O\end{smallmatrix}\!>\!N$. Fission of the ring readily occurs with alkali in the cold, the products are benzoic acid and benzonitrile, the latter probably from benzhydroxyamidoxime.

The author has not been successful in isolating other nitrile oxides. Ethyl chloro-oximino-acetate gave a quantitative yield of ethyl glyoxime peroxide dicarboxylate; an odour of nitrile oxide was, however, observed. Acethydroxamic chloride (this vol., i, 492) yielded a closely related acid, probably the compound, $OH\cdot CMe{:}NO\cdot CMe{:}NOH$.

W. R.

Termolecular Benzoyl Cyanide. OTTO DIELS and HUGO STEIN (*Ber.*, 1907, 40, 1655—1667. Compare Nef, Abstr., 1896, i, 71).—Termolecular benzoyl cyanide, $(BzCN)_3$, cannot be regarded as a cyanuric acid derivative (compare Nef, *loc. cit.*) for the following reasons. Only one carboxyl group has a ketonic function, since only a *monophenylhydrazone*, m. p. 226°, crystallising in colourless needles, can be obtained. Sodium methoxide eliminates one benzoyl group, giving a *substance* having the composition $(COPh\cdot CN)_2,HCN$ (I), which sinters at 350°, has m. p. 365° (decomp.), cannot be acylated or etherified, is not attacked by nitrous acid, and forms a colourless *sodium* salt, $C_{17}H_{12}O_3N_3Na$. Phosphoric acid at 180° converts (I) into a *substance*, $COPh\cdot CN,2HCN,H_2O$, (II), which crystallises in colourless leaflets, darkens at 220°, decomposes at 265°, and possesses both acid and basic properties, the latter being the more pronounced.

The yellow termolecular benzoyl cyanide, by solution in boiling glacial acetic acid or by the addition of concentrated hydrochloric acid to its solution in methyl ethyl ketone, is converted into a colourless *hydrate*, $3BzCN,H_2O$, (III), m. p. 185—186°, which does not react with phenylhydrazine, phenylcarbimide, or acetic anhydride, and which forms a yellow *ammonium* salt, $C_{24}H_{20}O_4N_4$. By heating termolecular benzoyl cyanide with acetic anhydride and zinc chloride for thirty minutes, the *compound*, $BzCN,2HCN,MeCO_2H$, (IV), is obtained in colourless needles, m. p. 226° (decomp.), sintering at 215°. By shorter heating with the same reagents, termolecular benzoyl cyanide yields the *substance*, $BzCN,2AcCN,MeCO_2H$, (V), m. p. 153°, sintering at 148°.

When (III) is treated with sodium methoxide, the *compound*,

$$2BzCN,HCN,H_2O,$$

(VI), m. p. 208—210°, is obtained, which forms a *sodium* salt,

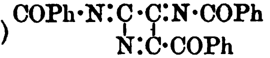
$$2BzCN,HCN,NaOH,$$

(VII), and is converted by boiling dilute sodium hydroxide into (I). Acetic anhydride and zinc chloride change (VI) into (IV); hence the two benzoyl groups in (III), which are eliminated by acetylation, are not similarly situated, since only one is displaced by the action of sodium methoxide.

When (VI) is treated in glacial acetic acid with nitrous fumes, or is oxidised by boiling acetic and chromic acids, *dibenzoyloxamide*,

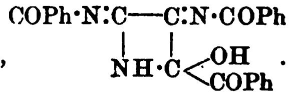
$$NHBz\cdot CO\cdot CO\cdot NHBz,$$

m. p. 214—215°, is obtained, identical with the substance prepared from ethyl oxalate and sodium benzamide. This reaction shows that in termolecular benzoyl cyanide two benzoyl groups attached to nitrogen are separated by the group C·C. The third carboxyl group of ketonic character is attached to carbon. The authors propose the formula (VIII)



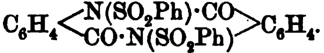
$$\begin{array}{l}COPh\cdot N{:}C\cdot C{:}N\cdot COPh\\ \qquad\qquad\quad | \quad\; | \\ \qquad\qquad\quad N{:}C\cdot COPh\end{array}$$

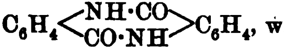
for termolecular benzoyl cyanide. The absence of colour in the hydrate (III) is due to the saturation of the double linking in the ring, formula (IX),



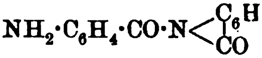
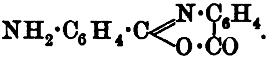
$$\begin{array}{l}COPh\cdot N{:}C\text{---}C{:}N\cdot COPh\\ \qquad\qquad\quad | \qquad | \\ \qquad\qquad NH\cdot C\begin{array}{l}<OH\\ <COPh\end{array}\end{array}.$$

C. S.

Bimolecular Anhydrides of Anthranilic Acid. Georg Schroeter (*Ber.*, 1907, 40, 1610—1621).—The author has already shown (Abstr., 1906, i, 415) that benzenesulphonylsulphanilic acid and benzenesulphonylnaphthionic acid respectively couple with diazotised *p*-nitroaniline to form azo-dyes, whilst diazo-salts are formed from other aromatic amines. This result led the author to test the behaviour of benzenesulphonylaminobenzoic acids in the same direction. Benzenesulphonylanthranilic acid was accordingly prepared by the action of benzenesulphonyl chloride on an alkaline solution of anthranilic acid; as a by-product, a substance was obtained which was insoluble in alkali and which investigation showed to be a bimolecular anhydride of benzenesulphonylanthranilic acid with the formula  $C_6H_4\left\langle\begin{matrix}N(SO_2Ph)\cdot CO\\ CO\cdot N(SO_2Ph)\end{matrix}\right\rangle C_6H_4$.

The compound is analogous to Anschütz's tetrasalicylide. The fundamental type of the bimolecular anhydride described is the hitherto unknown bimolecular anhydride,  $C_6H_4\left\langle\begin{matrix}NH\cdot CO\\ CO\cdot NH\end{matrix}\right\rangle C_6H_4$, which the author designates as dianthranilide. Attempts to prepare this are described. Water was eliminated from anthranoylanthranilic acid,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NH_2,$$

when a yellow anhydride was obtained, which is either the desired anhydride or anthranoylanthranil,  $NH_2\cdot C_6H_4\cdot CO\cdot N\left\langle\begin{matrix}C_6H_4\\ |\\ CO\end{matrix}\right.$ or  $NH_2\cdot C_6H_4\cdot C\left\langle\begin{matrix}N\cdot C_6H_4\\ \quad\ |\\ O\cdot CO\end{matrix}\right.$.

Benzenesulphonylanthranilic acid separates from 70% alcohol in needles, m. p. 223°.

p-*Benzenesulphonylaminobenzoic acid*, obtained by the action of benzenesulphonyl chloride on *p*-aminobenzoic acid, separates from 60% alcohol in silvery leaflets, m. p. 212°.

Dibenzenesulphonyldianthranilide separates from glacial acetic acid in needles, m. p. 264°. Determinations of its molecular weight by the cryoscopic method in phenol solution gave values agreeing with the formula $C_{26}H_{18}O_6N_2S_2$. When boiled with strong aqueous sodium hydroxide, it dissolves, and on acidification, benzenesulphonylanthranilic acid is precipitated. Derivatives of this acid are already described by Ullmann, Franke, and others.

Benzenesulphonylanthranilic chloride, $C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot COCl$, obtained by the action of phosphorus pentachloride on the acid, separates from benzene in crystals, which seem to be stable on exposure to air and which have m. p. 155°. The corresponding *amide* has m. p. 166—167°, and the *ethyl* ester has m. p. 92—93°. When the chloride is dissolved in pyridine, dibenzenesulphonyldianthranilide separates.

Ethyl o-*nitrobenzoylanthranilate*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Et$, obtained from *o*-nitrobenzoyl chloride and ethyl anthranilate in benzene solution, separates from alcohol in glistening, yellow prisms, m. p. 132°. When reduced by stannous chloride, it forms *ethyl anthranoylanthranilate*, $NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Et$, which separates from alcohol in yellow prisms, m. p. 105—106·8°. The analogous methyl ester has m. p. 115° (H. Meyer gives 118—119°), and its *hydrochloride* has m. p. 175—180°. When warmed with aqueous sodium hydroxide it forms *anthranoylanthranilic acid*, m. p. 203°.

When the latter acid is moistened with benzene and thionyl chloride added, *anthranoylanthranilic anhydride hydrochloride*, $C_{14}H_{11}O_2N_2Cl$, is formed, which, by the action of water or sodium hydroxide, is converted into the *compound*, $C_{14}H_{10}O_2N_2$; the latter forms canary-yellow needles, and has m. p. 162°.

Benzenesulphonylanthranoylanthranilic anhydride, obtained by the action of benzenesulphonyl chloride on the yellow anhydride, separates from alcohol or benzene in white needles, m. p. 214—215°.

Ethyl benzenesulphonylanthranoylanthranilate,

$$SO_2Ph\cdot NH\cdot C_6H_4\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2Et,$$

obtained from ethyl anthranilate and benzenesulphonylanthranilic chloride, separates from alcohol in needles, m. p. 132°. The corresponding *acid* has m. p. 222°, and when acted on by thionyl chloride, forms benzenesulphonylanthranoylanthranilic anhydride.

A. McK.

β-Alkylcinnamic Acids. II. GEORG SCHROETER [and, in part, HANS KESSELER, CARL OTTO LEVERKUS, and FRIEDRICH WÜLFING] (*Ber.*, 1907, **40**, 1589—1604. Compare Abstr., 1904, i, 415).—The method, previously used by the author for forming β-methylcinnamic acid from acetophenone and ethyl iodoacetate, is now found to be a general one for the preparation of β-alkylcinnamic acids. *p*-Methylacetophenone, propiophenone, butyrophenone, *iso*valerophenone, and phenyl amyl ketone respectively interact with ethyl iodoacetate and magnesium in benzene solution according to the equation: $Ar\cdot CO\cdot R + MgI\cdot CH_2\cdot CO_2Et \longrightarrow Ar\cdot CR\cdot(OMgI)\cdot CH_2\cdot CO_2Et$. The β-arylalkylhydracrylic acids, $Ar\cdot CR(OH)\cdot CH_2\cdot CO_2H$, obtained by decomposing the magnesium compound with water and then saponifying the ester, lose water with varying ease to form β-alkylcinnamic acids,

$$Ar\cdot CR\colon CH\cdot CO_2H.$$

It was sometimes found that when the crude ester,

$$OH\cdot CMePh\cdot CH_2\cdot CO_2Et,$$

was distilled, the elimination of water was not complete and an *acid*, $C_{20}H_{22}O_5$, was obtained, which separated from light petroleum in crystals, m. p. 62°; since this acid decolorised bromine and permanganate, it may be a molecular compound of β-phenylmethylhydracrylic acid and β-methylcinnamic acid. Generally, however, the elimination of water from β-phenylmethylhydracrylic acid proceeds in the normal manner with the formation of β-methylcinnamic acid, whilst β-methylstyrene and acetophenone are formed as by-products.

Methyl β-methylcinnamate has m. p. 28° and b. p. 152°/26 mm.; the *ethyl* ester has b. p. 162—163°/27 mm.

β-Methylcinnamic acid dibromide, $CMePhBr\cdot CHBr\cdot CO_2H$, obtained by the action of bromine on β-methylcinnamic acid, has m. p. 128° (decomp.). The *methyl ester dibromide*, $CMePhBr\cdot CHBr\cdot CO_2Me$, separates from light petroleum in prisms, m. p. 78—79°.

p-*Nitro-β-methylcinnamic acid*, $NO_2\cdot C_6H_4\cdot CMe\colon CH\cdot CO_2H$, obtained by nitrating β-methylcinnamic acid, forms yellow needles, m. p. 168—169°. When heated with dilute nitric acid in a sealed tube at 160°, it forms *p*-nitrobenzoic acid.

Ethyl p-*nitro-β-methylcinnamate*, $NO_2\cdot C_6H_4\cdot CMe:CH\cdot CO_2Et$, obtained by the nitration of ethyl β-methylcinnamate, has m. p. 74°. *Methyl* p-*nitro-β-methylcinnamate* has m. p. 121—122°. When *p*-nitro-β-methylcinnamic acid is reduced by ammonium sulphide it forms p-*amino-β-methylcinnamic acid*, $C_{10}H_{11}O_2N$, m. p. 124—125° (decomp.).

β-Phenylbutyric acid, $CHMePh\cdot CH_2\cdot CO_2H$, is obtained in a 98% yield by reducing β-methylcinnamic acid in aqueous alcoholic solution with 3% sodium amalgam; it has b. p. 168—169°/14 mm. and m. p. 39—40° (Kohler gives 47°). Its *methyl* ester has b. p. 133—134°/22 mm.

p-*Nitro-β-phenylbutyric acid*, $NO_2\cdot C_6H_4\cdot CHMe\cdot CH_2\cdot CO_2H$, obtained by nitrating the preceding acid, has m. p. 164°, and forms *p*-nitrobenzoic acid when oxidised by dilute nitric acid. Its *methyl* ester has m. p. 63—64°. p-*Amino-β-phenylbutyric acid*, obtained by reducing the nitro-acid with ammonium sulphide, has m. p. 176°.

o-p-*Dinitro-β-phenylbutyric acid*, $C_6H_3(NO_2)_2\cdot CHMe\cdot CH_2\cdot CO_2H$, obtained by nitrating the mononitro-acid with fuming nitric acid, forms glistening, yellow crystals, m. p. 139—140°. Its *methyl* ester has m. p. 61°. When the dinitro-acid is reduced by ammonium sulphide, a *compound*, $C_{10}H_{12}O_2N_2$, m. p. 177°, is formed.

p-β-Dimethylcinnamic acid, $C_6H_4Me\cdot CMe:CH\cdot CO_2H$, obtained from *p*-tolyl methyl ketone, ethyl iodoacetate, magnesium, and benzene, separates from carbon disulphide or light petroleum in rhombic prisms, m. p. 135° (Tiffeneau gives 136°). Its *methyl* ester has m. p. 46°.

β-Phenyl-β-ethylhydracrylic acid, $OH\cdot CEtPh\cdot CH_2\cdot CO_2H$, obtained from propiophenone, separates from benzene in needles, m. p. 122—123°. When acted on by concentrated sulphuric acid, it forms *β-ethylcinnamic acid*, $CEtPh:CH\cdot CO_2H$, which separates from light petroleum in glistening, rhombic plates, m. p. 95° and b. p. 172°/15 mm. Its *sodium* salt separates from acetone in glistening leaflets. Its *methyl* ester has b. p. 148°/22 mm. Its *dibromide* has m. p. 124—125° (decomp.). Its *mononitro*-derivative,

$$NO_2\cdot C_6H_4\cdot CEt:CH\cdot CO_2H,$$

separates from benzene in leaflets, m. p. 155°.

β-n-*Propylcinnamic acid*, $OH\cdot CPr^{\alpha}:CH\cdot CO_2H$, obtained from butyrophenone, has b. p. 183—184°/14 mm. and separates from light petroleum in transparent prisms, m. p. 94°.

β-Phenyl-β-iso*butylhydracrylic acid*,

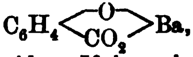
$$CHMe_2\cdot CH_2\cdot CPh(OH)\cdot CH_2\cdot CO_2H,$$

obtained from *iso*valerophenone, has m. p. 128—129° and contains $1H_2O$. *β*-iso*Butylcinnamic acid*, $CHMe_2\cdot CH_2\cdot CPh:CH\cdot CO_2H$, separates from aqueous alcohol in white crystals, m. p. 86°.

β-n-*Amylcinnamic acid*, $C_5H_{11}\cdot CPh:CH\cdot CO_2H,H_2O$, obtained from phenyl amyl ketone, separates from light petroleum, carbon disulphide, or dilute alcohol in long needles, m. p. 79—80·5°.

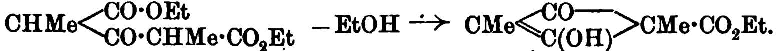
Phenyl amyl ketone, $C_6H_5\cdot CO\cdot C_5H_{11}$, obtained from hexoyl chloride, benzene, and aluminium chloride, has b. p. 132—134°/14 mm. and m. p. 27°. Its *semicarbazone* has m. p. 132°. A. McK.

Abietic Acid. FRANZ KORITSCHONER (*Zeitsch. angew. Chem.*, 1907, **20**, 641—645. Compare Fahrion, this vol., i, 329).—This investigation was carried out in order to decide whether abietic acid should be represented by the formula $C_{20}H_{30}O_2$ or $C_{19}H_{28}O_2$, and, further, whether the acid contains one carboxyl group or two hydroxyl groups. The electrical conductivity of an aqueous solution of the acid was determined, very small quantities of $N/10$ sodium hydroxide were then added successively, and the conductivity measured after each addition of the alkali. By plotting these conductivity values against the quantities of alkali added, a curve is obtained which shows a decided break. Since weak carboxylic acids, such as benzoic acid, give exactly similar curves, whereas phenols such as resorcinol give rounded curves without any break, it is evident that abietic acid is a carboxylic acid. That $C_{20}H_{30}O_2$ and not $C_{19}H_{28}O_2$ is the formula for this acid follows from the fact that the break in the abietic acid curve occurs at that point when the quantity of alkali added should be sufficient to completely neutralise the acid present, assuming the acid to possess the formula $C_{20}H_{30}O_2$. W. H. G.

Hydroxybenzoates. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1907, **144**, 756—757).—With the object of determining whether *p*-hydroxybenzoic acid could be transformed into salicylic acid, the author has studied the action of heat on barium *p*-hydroxybenzoate. The latter is not changed by prolonged heating at any temperature below 280°. Barium *p*-hydroxybenzoate, when heated at 280—281°, evolves carbon dioxide, probably owing to interaction with its water of crystallisation, thus: $(OH\cdot C_6H_4\cdot CO_2)_2Ba + 2H_2O = BaCO_3 + 2C_6H_5\cdot OH + CO_2 + H_2O$. The residue consists of a brown mass with a phenolic odour. It dissolves partially in cold water to a clear rose, in hot water to a hyacinth-red, in ammonia or potash to a clear red, in hydrochloric or acetic acid to a deep yellow, in dilute nitric acid to a brown, and in sulphuric acid to a clear red, solution. Neither benzoquinone nor diphenylene oxide are formed. If dry barium *p*-hydroxybenzoate is heated, the basic salt,  $C_6H_4<\substack{O\\CO_2}>Ba$, and phenol are formed with evolution of carbon dioxide. If by a is signified the amount of hydroxybenzoate dissolved by 10 c.c. of a solvent in one hour, then for barium *p*-hydroxybenzoate in water, $a_{18^\circ} = 1\cdot4$ gram; in methyl alcohol, $a_{16\cdot2^\circ} = 0\cdot37$ gram; in ethyl alcohol (95%), $a_{19\cdot5^\circ} = 0\cdot27$ gram.

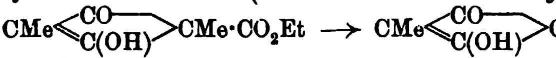
Under similar conditions, calcium *p*-hydroxybenzoate commences to evolve carbon dioxide at 245—246°. For this salt in water, $a_{20^\circ} = 1\cdot09$ gram; in ethyl alcohol (95%), $a_{18^\circ} = 1\cdot13$ gram. It combines with methyl alcohol at the ordinary temperature. Barium salicylate begins to evolve carbon dioxide at 250—251°; in water, $a_{18^\circ} = 0\cdot28$ gram; in methyl alcohol, $a_{18^\circ} = 0\cdot18$ gram; in ethyl alcohol, $a_{16\cdot5^\circ} = 0\cdot1\cdot333$ gram. Sodium salicylate first evolves carbon dioxide at 260—261°. E. H.

Formation of a Tetramethylene Ring by Condensation of *s*-Ethyl Dimethylacetonedicarboxylate. GEORG SCHROETER and C. STASSEN (*Ber.*, 1907, **40**, 1604—1610).—The authors find that *s*-ethyl dimethylacetonedicarboxylate, when dissolved in concentrated sulphuric acid, forms, after twenty hours at the ordinary temperature, the *acid*, $C_9H_{12}O_4$. The latter is probably ethyl 1 : 3-dimethyl*cyclo*butene-4-ol-2-one-1-carboxylate (ethyl *aci*-dimethyldiketo*cyclo*butanecarboxylate) and its formation is represented by



$$\mathrm{CHMe}\Big<\begin{matrix}\mathrm{CO\cdot OEt}\\ \mathrm{CO\cdot CHMe\cdot CO_2Et}\end{matrix} - \mathrm{EtOH} \rightarrow \mathrm{CMe}\Big<\!\!\!<\begin{matrix}\mathrm{CO}\text{——}\\ \mathrm{C(OH)}\end{matrix}\Big>\mathrm{CMe\cdot CO_2Et}.$$

It separates from dilute alcohol in colourless needles, m. p. 133—135°. It is a monobasic acid, and may be titrated sharply with sodium hydroxide, using phenolphthalein as indicator. Determinations of the molecular weight by the cryoscopic method in phenol and glacial acetic acid solutions respectively gave values corresponding with the formula $C_9H_{12}O_4$. Its *sodium* salt is a colourless powder. The acid itself is somewhat unstable, and after a time is transformed into an oil. The acid decolorises alkaline permanganate at once and also decolorises a solution of bromine in chloroform. It combines, although not with ease, with phenylhydrazine, hydroxylamine, and semicarbazide respectively. When boiled with aqueous barium hydroxide, it loses carbon dioxide, and is converted into 1 : 3-*dimethyl*cyclo*butene*-4-*ol*-2-*one* (aci-2 : 4-*diketo*-1 : 3-*dimethyl*cyclo*butane*), thus:



$$\mathrm{CMe}\Big<\!\!\!<\begin{matrix}\mathrm{CO}\text{——}\\ \mathrm{C(OH)}\end{matrix}\Big>\mathrm{CMe\cdot CO_2Et} \rightarrow \mathrm{CMe}\Big<\!\!\!<\begin{matrix}\mathrm{CO}\text{——}\\ \mathrm{C(OH)}\end{matrix}\Big>\mathrm{CHMe},$$

which separates from benzene in crystals, m. p. 135°, and is a monobasic acid.

When the sodium salt of the acid, $C_9H_{12}O_4$, is boiled with an ethyl-alcoholic solution of methyl iodide for three hours, it is converted into *ethyl trimethylacetonedicarboxylate*, $CO_2Et\cdot CHMe\cdot CO\cdot CMe_2\cdot CO_2Et$, which boils at 132—133°/12 mm. It does not give a violet coloration with ferric chloride, and is not condensed by concentrated sulphuric acid. A. McK.

4-Hydroxydeoxybenzoin-3-carboxylic Acid. FRITZ GLASSNER (*Monatsh.*, 1907, **28**, 281—295. Compare Weisl, Abstr., 1905, i, 904).—Attempts to condense phenylacetic acid with the three hydroxybenzoic acids or phenylacetyl chloride with *o*- and *m*-hydroxybenzoic acids in presence of aluminium chloride were unsuccessful. The action of phenylacetyl chloride on salicylic acid in nitrobenzene solution at 70° leads to the formation of an *acyl* compound which will be described later, but in presence of aluminium chloride to the formation of 4-*hydroxydeoxybenzoin*-3-*carboxylic acid*, $CH_2Ph\cdot CO\cdot C_6H_3(OH)\cdot CO_2H$. This crystallises from dilute alcohol in colourless, rectangular plates, m. p. 224°, gives a cherry-red coloration with alcoholic ferric chloride, and yields carbon dioxide and *p*-hydroxydeoxybenzoin when heated with water at 180—200°, or toluene and 4-hydroxy*iso*phthalic acid when heated with 70% potassium hydroxide at 170—200°. The *sodium* ($\frac{1}{2}H_2O$) and *silver* salts of the keto-acid are described; the *acetyl* derivative, $C_{17}H_{14}O_5$, crystallises in needles, m. p. 140°, and is hydrolysed by boiling water; the *oxime*, $C_{15}H_{13}O_4N$, m. p. 170°, gives a dark blue coloration with alcoholic ferric chloride, and is partially hydrolysed by boiling water, forming the keto-acid. The action of 7·5 atoms of bromine on 1 mol. of the keto-acid in glacial acetic acid solution leads to the formation of *dibromo*-4-*hydroxydeoxybenzoin*,

$$CH_2Ph\cdot CO\cdot C_6H_2Br_2\cdot OH,H_2O,$$

which crystallises in monoclinic prisms [$a:b:c = 1\cdot6772:1:1\cdot3627$; $\beta = 97°24'$], m. p. 138—142°, and does not give a coloration with ferric chloride. The *ammonium*, *sodium*, *potassium*, *silver*, and *barium* derivatives of the dibromo-compound are described.

The action of iodine on the keto-acid in alkaline solutions leads to the formation of a small amount of a *product* crystallising in needles, m. p. 139—147°, whilst in ammoniacal solution two *products* are formed; one of these forms a sparingly soluble *ammonium* salt, crystallising in needles, m. p. 48°, and decomposing gradually at the ordinary temperature. The second product crystallises when precipitated by hydrochloric acid from its solution in alcoholic potassium hydroxide, decomposes at 279°, and contains nitrogen. G. Y.

Nitrated Phenylglutaric Acids. III. HANS MEERWEIN and GEORG SCHROETER (*Ber.*, 1907, **40**, 1586—1589. Compare Abstr., 1902, i, 544; 1903, i, 831).—It was stated formerly by the authors that *o*-nitro-β-phenylglutaric acid is converted into an isomeric *iso*-*o*-nitro-β-phenylglutaric acid by means of ammonium sulphide. This observation is now found to have been incorrect, since the *o*-nitro-β-phenylglutaric acid formerly used contained from 15% to 20% of the meta-isomeride; the latter was reduced by the ammonium sulphide, whilst the former was not.

m-*Aminophenylglutaric acid*, $C_{11}H_{13}O_4N$, obtained from the mother liquors of the reduction of crude *o*-nitrophenylglutaric acid by stannous chloride, separates from water in needles, m. p. 214·5° (decomp.); its *dimethyl* ester separates from a mixture of benzene and light petroleum in transparent octahedra, m. p. 46°. That the acid in question is the meta-isomeride is shown by its identity with the product of the reduction of *m*-nitro-β-phenylglutaric acid, obtained by the condensation of *m*-nitrobenzaldehyde and ethyl acetoacetate.

Crude *o*-nitrophenylglutaric acid may be purified either by means of ammonium sulphide or by fractionation of its methyl ester, or by oxidation with permanganate. The latter reagent attacks the meta-acid more readily than it does the ortho-acid.

The solubility in water of the crude *o*-nitrophenylglutaric acid (m. p. 176°) was also determined and compared with that of the pure ortho-acid (m. p. 205°) and of the pure meta-acid (m. p. 204°), and of a mechanical mixture of the two. The latter mixture (70% ortho-acid and 30% meta-acid) had the same melting point (177°) as that of the crude ortho-acid.

When β-phenylglutaric acid is nitrated under the conditions formerly quoted (*loc. cit.*), about 50% of *p*-nitrophenylglutaric acid, about 38% of *o*-nitrophenylglutaric acid, and about 12% of *m*-nitrophenylglutaric acid are produced. The para-acid may easily be separated, as it is sparingly soluble in water. The meta- and ortho-acids, however, are not readily separated by fractional crystallisation. The ortho-acid may be obtained (1) from the dimethyl esters (resulting from the mixture of ortho- and meta-acids) by means of a mixture of ether and petroleum, (2) by oxidation of the mixture with permanganate, or (3) by ammonium sulphide, the latter method being the most convenient of the three. A. McK.

Preparation of Aromatic Hydroxy-aldehydes. PHILIPPE CHUIT (*Bull. Soc. ind. Mulhouse*, 1907, 72—73) and JULES DEMANT (*ibid.*, 73—74).—In Reimer's synthesis of hydroxy-aldehydes, by heating phenols with chloroform in aqueous or aqueous-alcoholic solution, the greater part of the product is resinified by the hot alkali; thus in the preparation of vanillin from guaiacol in aqueous-alcoholic solution, although the reaction takes place almost completely, the yield of hydroxy-aldehyde is not more than 10% of the phenol, and much resin is formed. Chuit proposes to avoid this disadvantage by carrying out the reaction in cold aqueous alkaline solution, the liquids being mixed by energetic stirring. In this manner he obtains vanillin in a yield of 20% of the guaiacol, accompanied by small amounts of *m*-methoxysalicylaldehyde and by only very little resin. The unchanged guaiacol and chloroform are recovered readily.

Following Tiemann and Koppe's instructions (Abstr., 1882, 54), Demant has obtained vanillin in a 33·7% yield and regained 47·5% of the guaiacol, whilst under Chuit's conditions he obtains only 22·5% of vanillin and 50% of regained guaiacol. G. Y.

Behaviour of Organo-magnesium Compounds towards Oximes and their *O*-Ethers. MAX BUSCH and RICHARD HOBEIN (*Ber.*, 1907, **40**, 2096—2099).—The action of alkyl magnesium bromides on oximes leads, in the first place, to the substitution of the hydroxyl group by alkyl, and subsequent formation of an additive compound, $CHRR'\cdot NR'\cdot MgBr$. Similarly, *C*-alkoxyl groups are also replaced by alkyl, since *O*-ethers of the oximes yield the same secondary bases. From α-benzaldoxime and magnesium phenyl bromide, the hydrochloride of anilinodiphenylmethane, $CHPh_2\cdot NHPh$, is obtained (compare Busch and Rinck, Abstr., 1905, i, 519). α-Benzaldoxime and magnesium α-naphthyl bromide give rise only to the intermediate substitution product, benzylidene-α-naphthylamine. The methyl and benzyl ethers of α-benzaldoxime yield the same products as the oxime. These reactions are in no case simple, a very considerable proportion of by-product being formed. E. F. A.

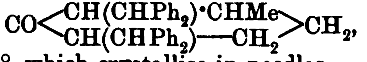
Reaction between Unsaturated Compounds and Organic Magnesium Compounds. XI. Cyclic Ketones. ELMER P. KOHLER (*Amer. Chem. J.*, 1907, **37**, 369—392).—Experiments have been carried out with three types of unsaturated cyclic ketones, namely, those containing unsaturated side-chains, those having an unsaturated nucleus, and those with two ethylene linkings, one in the nucleus and the other in the side-chain.

By the addition of pulegone, a ketone of the first type, to magnesium methyl iodide, Grignard (Abstr., 1901, i, 681) obtained a hydrocarbon, evidently formed by loss of water from an intermediate alcohol. Since, however, ketones of this type generally behave like the corresponding open-chain compounds, it seemed probable that the result was due to the presence of the two methyl groups attached to one of the unsaturated carbon atoms, and this view has been confirmed by examining the behaviour of dibenzylidenemethyl*cyclo*hexanone which has been found to react in the same way as dibenzylideneacetone.

The reaction with ketones of the second type has been studied by

Bamberger and Blangley (Abstr., 1903, i, 557), and by Auwers and Keil (Abstr., 1903, i, 620). In both cases, 1 : 2-additive compounds were obtained. It is evident that 1 : 4-compounds are not obtained with the simplest ketones of this type, and an attempt was therefore made to ascertain whether a different result would be obtained with ketones in which the reactivity of the carboxyl group is diminished by substituents in the *a*-position. Carvone was chosen for this purpose, but just as the work on this substance was completed, the papers of Rupe and Liechtenhan (Abstr., 1906, i, 374), and Klages and Sommer (*ibid.*, 1906, i, 566) appeared. The author's results confirm those of Rupe and Liechtenhan, but their assumption that the reaction takes place by 1 : 2-addition is incorrect, compounds obtained by the action of Grignard's reagent on such ketones being formed by 1 : 4-addition. This is proved conclusively by experiments with diphenyl*cyclo*hexanone, which behaves towards Grignard's reagent in the same way as unsaturated open-chain compounds.

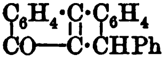
By the action of magnesium phenyl bromide on dibenzylidenemethyl*cyclo*hexanone, two isomeric *ketones*, $C_{27}H_{26}O$, m. p. 192° and 132°, crystallising in needles, are produced together with a third *compound*, m. p. 154—156°, which was not obtained in sufficient quantity for analysis. The isomeric ketones give orange-coloured solutions in strong sulphuric acid, decolorise bromine solution, and reduce potassium permanganate. When oxygen is passed through the ethereal solution, obtained from the decomposition of the magnesium derivative from dibenzylidenemethyl*cyclo*hexanone with cold hydrochloric acid, isomeric *peroxides*, $C_{27}H_{26}O_3$, m. p. 176° and 142°, are obtained, which crystallise in colourless needles. Each of the isomeric ketones reacts with magnesium phenyl bromide with formation of two stereoisomeric *tetraphenyltrimethyl*cyclo*hexanones*,



$$CO\left<\begin{matrix}CH(CHPh_2)\cdot CHMe\\ CH(CHPh_2)\text{—}CH_2\end{matrix}\right>CH_2,$$

m. p. 282° and 190°, which crystallise in needles.

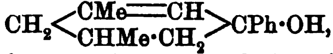
Diketobenzylidenehydrindene

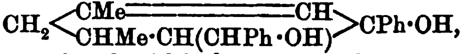


reacts with magnesium phenyl bromide in an unexpected manner with formation of a *ketone*, m. p. 162°, which separates from alcohol in yellow plates and, on oxidation with potassium permanganate, is converted in an *acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CHPh\cdot CO_2H,$$

m. p. 131—133°, which crystallises in flat, colourless needles. The name "bindene" is suggested for the hydrocarbon from which the ketone is derived, the ketone itself being "6-phenylbindene-8-one."

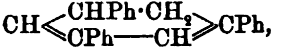
*Phenyldimethyl*cyclo*hexanol*,  $CH_2\left<\begin{matrix}CMe\text{=}CH\\ CHMe\cdot CH_2\end{matrix}\right>CPh\cdot OH$, m. p. 111°, obtained by the action of magnesium phenyl bromide on dimethyl*cyclo*hexanone, separates from ether in large, colourless plates. When benzylidenedimethyl*cyclo*hexanone is treated with magnesium phenyl bromide, a *compound*, probably



$$CH_2\left<\begin{matrix}CMe\text{=}CH\\ CHMe\cdot CH(CHPh\cdot OH)\end{matrix}\right>CPh\cdot OH,$$

m. p. 106°, is produced, which forms large, lustrous tables, and on oxidation with permanganate yields benzoic acid.

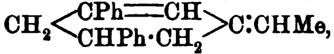
[With **Mary Violet Dover.**]—In preparing diphenyl*cyclo*hexanone by the action of ethyl acetoacetate on benzylideneacetophenone as described by Knoevenagel and Schmidt (*Annalen*, 1894, **281**, 59), it was found that the additive compound obtained when sodium ethoxide is used as the condensing agent is not identical, but isomeric, with that obtained when diethylamine is employed; the former has m. p. 168°, and the latter, m. p. 121°. Diphenyl*cyclo*hexanone has m. p. 83^{c} (not 70—72° as stated by Knoevenagel and Schmidt, *loc. cit.*). The *oxime*, m. p. 163—164°, crystallises in needles. By the action of magnesium phenyl bromide on the ketone, *triphenyl*cyclo*hexadiene*,



$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CHPh\cdot CH_2}\\ \mathrm{CPh{-}{-}CH}\end{matrix}\right\rangle\mathrm{CPh},$$

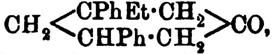
m. p. 111°, is produced, which on oxidation with potassium permanganate is converted into 1 : 3 : 5-triphenylbenzene.

The products of the action of a large excess of magnesium ethyl bromide on diphenyl*cyclo*hexanone are *diphenylethylidene*cyclo*hexene*,



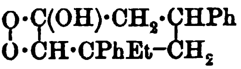
$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CPh{=}{=}CH}\\ \mathrm{CHPh\cdot CH_2}\end{matrix}\right\rangle\mathrm{C{:}CHMe},$$

b. p. 152°/22 mm., and *diphenylethyl*cyclo*hexanone*,



$$\mathrm{CH_2}\left\langle\begin{matrix}\mathrm{CPhEt\cdot CH_2}\\ \mathrm{CHPh\cdot CH_2}\end{matrix}\right\rangle\mathrm{CO},$$

b. p. 170°/24 mm. When diphenylethylidene*cyclo*hexene is oxidised with potassium permanganate, it is converted into γ-benzoyl-β-phenylbutyric acid, the *methyl* ester of which has m. p. 94°. It has been proved that the diphenylethyl*cyclo*hexanone is formed by 1 : 4-addition by treating it with magnesium ethyl bromide, when *diphenylethyl*cyclo*hexanol peroxide*, m. p. 269—270°, is produced, which forms small, hard prisms. If diphenyl*cyclo*hexanone is treated with an equivalent quantity, instead of excess, of magnesium ethyl bromide, the same hydrocarbon is produced, but instead of the ketone a *compound*, $C_{38}H_{38}O_2$, m. p. 256°, is obtained, which is similar to the substances formed from unsaturated, open-chain ketones. E. G.



1-Chloroacetyl-2 : 4-dichlorobenzene. **Franz Kunckell** (*Ber.*, 1907, **40**, 1702—1703).—The interaction of *m*-dichlorobenzene, chloroacetyl chloride, and aluminium chloride in carbon disulphide on the water-bath, results in the formation of 1-*chloroacetyl*-2 : 4-*dichlorobenzene*, $C_8H_5OCl_3$, crystallising in long, pale yellow prisms, m. p. 57°. The position of the chloroacetyl residue was determined by oxidation with potassium permanganate to the corresponding dichlorobenzoic acid.

p-Dichlorobenzene does not react with chloroacetyl chloride under the above conditions. W. R.

Reduction of Ketones by Alcoholic Stannous Chloride and Hydrochloric Acid. Correction. **Hermann Apitzsch** (*Ber.*, 1907, **40**, 1803—1804. Compare Apitzsch and Metzger, Abstr., 1904, i, 510; Klages, Abstr., 1906, i, 674.).—Benzoin is not reduced by alcoholic stannous chloride and hydrochloric acid; benzil is, however, reduced to benzoin, and the same product is formed when benzoin-anilide or ethylbenzoin is heated with the reducing agents at

150—170°. Cuminoin and benzylideneacetophenone are not reduced. Anisoin and anisil both yield deoxyanisoin and not *iso*hydroanisoin.

J. J. S.

The Benzil Reaction. ARTHUR HANTZSCH and WALTER H. GLOVER (*Ber.*, 1907, **40**, 1519—1523. Compare Liebermann and Homeyer, Abstr., 1880, 259; Bamberger, Abstr., 1885, 807; Bamberger and Scholl, Abstr., 1899, i, 701).—This work was undertaken with the object of throwing light on the constitution of the violet products formed by the action of potassium ethoxide on benzil and on a mixture of benzil and benzoin. Bamberger and Scholl's assumption that the products are identical (*loc. cit.*) cannot be correct, since whilst 4:4′-dichlorobenzil gives no coloration with cold alcoholic-aqueous potassium hydroxide, but a purple-red on boiling, 4:4′-*dichlorobenzoin*, colourless needles, m. p. 88°, gives at the ordinary temperature a greenish-blue coloration becoming blue gradually on boiling, and mixtures of 4:4′-dichlorobenzoin with benzil and with 4:4′-dichlorobenzil give a deep-blue coloration with either the cold or the hot alkali. Moreover, the coloration obtained on adding potassium hydroxide to an alcoholic solution of benzil and benzoin disappears on shaking, whereas that formed by boiling benzil with alcoholic potassium hydroxide is stable.

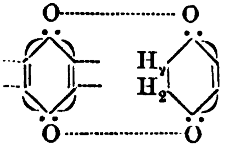
When treated with a concentrated ethereal solution of potassium ethoxide, benzil yields a small amount of benzilic acid and a blue solution, which on evaporation in a vacuum deposits an indigo-blue mass, decolorised by air. It is shown that this potassium compound is not decomposed by water and therefore cannot be analogous to Beckmann and Paul's blue sodium salt formed by the action of sodium on benzil in ethereal solution. By treating the concentrated, deep-red, aqueous solution of the potassium compound with carbon dioxide, a small amount of a *product*, $C_{28}H_{20}O_4$, is obtained as a yellow powder, m. p. 65—67°; this is considered to be the *aldol* of benzil, $COPh \cdot CPh(OH) \cdot C_6H_4 \cdot CO \cdot COPh$. In concentrated aqueous solution, its potassium derivative is intense blue by reflected, deep-red by transmitted, light. An indigo-blue, acid *barium* salt is described.

The aldol does not appear to be an intermediate product in the conversion of benzil into benzilic acid (compare Montagne, Abstr., 1902, i, 473).

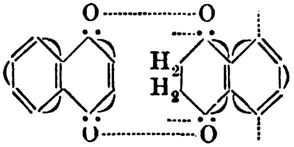
G. Y.

Decahydro-α-naphthyl Ketone and Decahydro-α-naphthylamine. HENRI LEROUX (*Compt. rend.*, 1907, **144**, 981—983. Compare Abstr., 1905, i, 601; 1906, i, 16).—*Decahydro-α-naphthyl ketone*, m. p. 32°, obtained by oxidising decahydro-α-naphthol with chromic acid, crystallises from light petroleum in bulky, prismatic tablets, has an odour like that of menthol, and yields a crystalline *additive product* with sodium hydrogen sulphite. The *semicarbazone*, m. p. 230° (approx.), forms colourless needles; the *phenylhydrazone* is amorphous; the *oxime*, m. p. 165°, crystallises from alcohol, sublimes at 100°, forming long, colourless needles, and on reduction with sodium in alcohol yields *decahydro-α-naphthylamine*, b. p. 96—97°/14 mm. This is a colourless, unpleasant-smelling liquid, which absorbs carbon dioxide on exposure to air. The *hydrochloride*, m. p. 190° (decomp.), *platinichloride*, and *picrate*, m. p. 210° (decomp.), are crystalline. The *acetyl* derivative, m. p. 182°, forms slender needles from alcohol and sublimes at 125°. The *benzoyl* derivative, m. p. 195°, crystallises in slender needles from alcohol and sublimes at 150°. T. A. H.

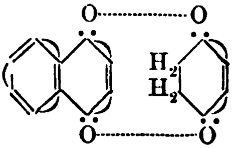
Mixed Quinhydrones. GUSTAV URBAN (*Monatsh.*, 1907, **28**, 299—318).—It was shown by Biltris (Abstr., 1897, i, 199) that the action of benzoquinone on thymoquinol leads to the immediate formation of quinol and thymoquinone together with small amounts of the mixed quinhydrone. It follows that thymoquinol is oxidised to thymoquinone more easily than quinol to benzoquinone. The present work was undertaken to compare in this manner the relative ease with which a-naphthaquinol and quinol are oxidised to a-naphthaquinone and benzoquinone respectively, and at the same time to compare the mixed quinhydrones formed, on the one hand, from a-naphthaquinol and benzoquinone and, on the other, from quinol and a-naphthaquinone. It is found that whilst a mixed quinhydrone is formed directly from a-naphthaquinone and quinol in molecular proportions in ethereal light petroleum solution, the same compound is obtained from a-naphthaquinol and benzoquinone; its formation in this case being preceded by that of a-naphthaquinone and quinol. The constitution of the quinhydrones is discussed in the light of Thiele's theory of partial valencies, and the following tautomeric structural formulæ are ascribed to ordinary quinhydrone (I), to a-naphthaquinhydrone (II), and to the mixed quinhydrone from a-naphthaquinone and quinol (III).



(I.)



(II.)



(III.)

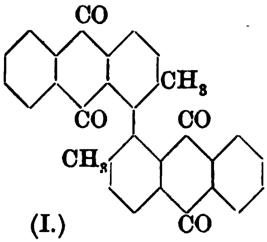
The mixed *quinhydrone*, $C_{16}H_{12}O_4$, crystallises from a mixture of ether and light petroleum in negatively doubly refracting, rhombic leaflets or needles [$a:b:c = 0.4590:1:0.2929$]; m. p. 123°, is a dark green by reflected, red by transmitted, light, and is decomposed into a-naphthaquinone and quinol on solution in alcohol, ether, or light petroleum, but can be recrystallised unchanged from glacial acetic acid.

The action of 2 mols. of benzoquinone on 1 mol. of a-naphthaquinol in warm glacial acetic acid solution leads to the formation of ordinary quinhydrone which crystallises out, a-naphthaquinone remaining in solution. On mixing 1 mol. of benzoquinone with 2 mols. of a-naphthaquinol in warm glacial acetic acid solution, a-naphthaquinhydrone crystallises out and quinol remains in the mother liquor.

G. Y.

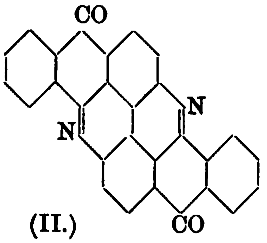
Dianthraquinonyl and its Derivatives. BADISCHE ANILIN- UND SODA-FABRIK (D.R.-P. 180157).—It is well known that metallic copper is a useful condensing agent for the halogenated derivatives of benzene and naphthalene and this reaction has now been applied in the production of quinones in the anthracene series. 2 : 2′-Dimethyl-1 : 1′-dianthraquinonyl is thus prepared by heating an intimate mixture of 1-iodo-2-methylanthraquinone and copper powder at 210°. The product crystallises from xylene in yellowish-brown prisms which are soluble in aniline or nitrobenzene. G. T. M.

Constitution and Synthesis of Flavanthrene. Roland Scholl (*Ber.*, 1907, **40**, 1691—1702).—*Flavanthrene* is obtained from 2-aminoanthraquinone by heating with molten potassium hydroxide at 350° (D.R.-P. 136015), with aluminium chloride (138119), heating with antimony pentachloride in boiling nitrobenzene (139633), or by acid oxidising materials such as chromic acid (141355); in the latter case it is accompanied by indanthrene. It is a yellow dye, which gives a dark blue bath on reduction with alkaline hyposulphite. Unmordanted vegetable fibres are coloured deep blue in this bath, and on exposure to the air for a few minutes they become yellow (D.R.-P. 139835, 140573, 142963, 139633). Flavanthrene is a weak base, very sparingly soluble in solvents of high boiling point, and towards heat it is very stable.



(I.)

[With Karl Holdermann, Johannes Mansfeld, and Max. A. Kunz.]—The constitution of flavanthrene has been determined by its synthesis from 1-amino-2-methylanthraquinone (Abstr., 1883, 70). The first step was the preparation of 1-*iodo*-2-*methylanthraquinone*, $C_{15}H_9O_2I$, from the amino-compound by the diazo reaction, it crystallises in brown leaflets, m. p. 169—169·5°. This was converted into 2 : 2′-*dimethyl*-1 : 1′-*dianthraquinonyl* (I) by Ullmann's copper method (Abstr., 1904, i, 725), the temperature employed being 270°. The mass obtained is first treated with benzene to remove dark coloured impurities, then reduced with alkaline hyposulphite, and filtered to remove copper and copper iodide, the dimethyldianthraquinonyl being precipitated by blowing air through the filtrate, and finally crystallised from xylene; it forms yellowish-brown needles, m. p. 366—367° (corr.). It was also obtained by Knoevenagel's method from the diazonium sulphate of the methylanthraquinone by means of copper powder and acetic anhydride (Abstr., 1895, i, 669). On oxidation with chromic acid and glacial acetic acid, 1 : 1′-*dianthraquinonyl*-2 : 2′-*dicarboxylic acid*, $C_{30}H_{14}O_8$, is obtained, crystallising in yellowish-brown crystals, m. p. 334—337° (decomp.). The *amide*, $C_{30}H_{16}O_6N_2$, was next obtained in pale yellow crystals, and converted into flavanthrene by means of potassium hydroxide and bromine. The dye must therefore have the annexed constitution (II), and in obtaining it from 2-aminoanthraquinone, 2 molecules must unite with loss of 2 molecules of water and 2 atoms of hydrogen.



(II.)

[With CARL STOLL.]—1 : 3-*Dibromo-2-aminoanthraquinone*, $C_{14}H_7O_2NBr_2$, obtained by shaking the aminoanthraquinone with bromine and water for nine hours, crystallises from glacial acetic acid in yellowish-brown prisms, m. p. 239°. Its *diacetate*, $C_{18}H_{11}O_4NBr_2$, m. p. 202°, forms greenish-yellow crystals, and when heated with copper powder at 200° gives 2-*diacetylaminoanthraquinone*, m. p. 258°, instead of the 3 : 3′-dibromo-2 : 2′-diamino-1 : 1′-dianthraquinyl expected. W. R.

Crystallographic Constants of Some Organic Compounds. ARRIEN JOHNSEN (*Jahrb. Min.*, 1907, i, 89—106).—Crystals of the following are described. Pyrazole methiodide; furylhydrophenanthraquinone; optically active camphorylhydroxylamine; optically active camphorylhydroxylamine and its ethyl ester; *i*-bromomalic acid; *i*-*iso*bromomalic acid; *i*-chloromalic acid; oxycitraconic acid; *i*- α- and β-bromocitramalic acids; *i*-chlorocitramalic acid; platodiethylamine chloride, bromide and nitrate; active benzoylcamphorylhydroxylamine; potassium *o*-chlorophenol-*p*-sulphonate; bromostrychnine; succinylhydroxylamine; *i*- α- and β-methylmalic acids; methyl tetraphenylenesuccinate; *iso*bromometacrylic acid; chloral hydrosulphide; magnesium *d*-tartrate, and hydrogen magnesium *d*-tartrate. L. J. S.

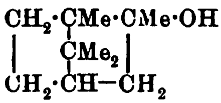
Terpenes and Ethereal Oils. LXXXIII. OTTO WALLACH and HEINRICH WIENHAUS (*Annalen*, 1907, **353**, 209—227).—I. *Observations in the Fenchone Series.*—Fenchone semicarbazone, obtained by Rimini (Abstr., 1900, i, 554) from *iso*pernitrosofenchone, is formed by the action of semicarbazide hydrochloride and sodium acetate on *d*- or *l*-fenchone in aqueous-alcoholic solution at the ordinary temperature in about two weeks; it crystallises from dilute alcohol in long, stout, rhombic prisms, m. p. 182—183° (186—187°: Rimini, *loc. cit.*). *d*-Fenchone semicarbazone, $[\alpha]_D$ +47·04°; *l*-fenchone semicarbazone, $[\alpha]_D$ −46·88°; *r*-fenchone semicarbazone, m. p. 172—173°, crystallises with difficulty. It is found that *l*-fenchone, prepared from thuja oil (Abstr., 1893, i, 105; 1898, i, 486), contains *l*-camphor and yields a mixture of *l*-camphor semicarbazone, m. p. 238°, $[\alpha]_D$ −39·9°, and *l*-fenchone semicarbazone. The *l*-camphor is not present in the thuja oil, as the fractions, b. p. 200—220°, yield α-thujone semicarbazone, but not camphor semicarbazone until after hydrolysis and oxidation (compare Abstr., 1905, i, 147). The source of the *l*-camphor, therefore, is considered to be *l*-borneol esters present in the thuja oil.

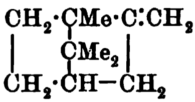
Commercial *d*-fenchone contains *d*-camphor, as it yields *d*-camphor semicarbazone, m. p. 238° (Tiemann, Abstr., 1895, i, 675); a small amount of substance, m. p. 245°, obtained on recrystallisation, is not the pure semicarbazone (compare Rimini, *loc. cit.*).

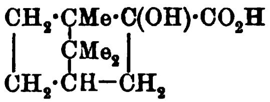
The camphor cannot be removed from *d*- or *l*-fenchone by energetic treatment with nitric acid, but the pure fenchones may be obtained by acting on the mixtures with semicarbazide for two days and distilling the fenchone with steam; the camphor remains in the distillation residue as the semicarbazone.

It has been found previously that several isomeric fenchones are obtained from fenchyl alcohol, whilst analogous observations have been made in the camphene series by Moycho and Zienkowski (Abstr., 1905, i, 710). Hence it seemed desirable to investigate the behaviour in this respect of a homologue of fenchyl alcohol. Homofenchyl alcohol (α-methylfenchol), $C_7H_{12}\!<\!\begin{matrix}CHMe\\ CMe\cdot OH\end{matrix}$ (Zelinsky, Abstr., 1901, i, 660), m. p. 61°, b. p. 215—216°, $[\alpha]_D$ +1·12—+2·2°, when heated with potassium hydrogen sulphate at 160°, yields *homofenchene*, $C_{11}H_{18}$, m. p. 32—37°, b. p. 170—172°, D 0·8520, n_D^{46-47} 1·4557, $[\alpha]_D$ +23·06°, which contains an ethylene linking and closely resembles camphene. On oxidation with potassium permanganate, a crude homofenchene, obtained from fenchone containing camphor, yielded small amounts of *homocamphenylic acid*, derived from camphene, and of a hydroxylactone (?), $C_{11}H_{16}O_3$, m. p. 157°. This oxidation is to be repeated with a homofenchene derived from pure fenchone.

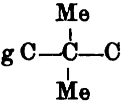
II. *Homocamphene and Homocamphenylic* (*α-Borneolcarboxylic*) *Acid.*—*Homocamphene*, m. p. 28°, b. p. 166—168°, obtained by heating the product of the action of magnesium methyl iodide on camphor with potassium hydrogen sulphate, resembles camphene. On oxidation with potassium permanganate it yields *homocamphenylic* (*α-borneolcarboxylic*) *acid*, $OH\cdot C_{10}H_{16}\cdot CO_2H$, which crystallises in stout needles, m. p. 179°, $[\alpha]_D$ −30·72—−34·8°, and forms a sparingly soluble *sodium* salt; the *silver* salt was analysed. As homocamphenylic acid yields camphor when heated with lead dioxide and dilute sulphuric acid, the following formulæ are suggested:


Homoborneol.


Homocamphene.


Homocamphenylic Acid.

(compare Bredt and Burkheiser, Abstr., 1906, i, 680). G. Y.

Constitution of the Terpenes. GUSTAV WENDT (*Pharm. Zeit.*, 1907, 52, 331—332).—A number of new formulæ for various terpenes are proposed without, however, adducing any experimental evidence in support of them. The main feature of the formulæ is that they all contain the grouping  $C\!-\!\overset{Me}{\underset{Me}{C}}\!-\!C$ in which the central or so-called "pure" carbon atom is surrounded by four others. P. H.

The Terpene Oils of Manila Elemi. ALPHONSO M. CLOVER (*Philippine J. Sci.*, 1907, 2, 1—40).—The resins obtained from twenty-one specimens of *Canarium luzonicum* have been investigated. The resin from each tree was worked up separately, as a preliminary examination indicated that the terpenes obtained from the resins of different trees varied considerably. The resin was heated in a flask placed in an oil-bath at 125—150°, and the terpenes distilled under a pressure of 10—15 mm. A second distillate was collected when the temperature was raised to 200°, and heavy oils were collected from 200—230° or 200—250°. No changes appear to occur at these temperatures. Of the twenty-one samples, ten gave pure *d*-limonene, and nine contained more or less phellandrene. Several of the latter also contained *l*-limonene and probably another terpene of the limonene series. Pinene does not appear to be present.

The remaining two samples of resin gave terpenes which were practically inactive, and these proved to be terpinene and terpinolene. The terpinolene extracted from the fresh resin is practically pure, but when kept for some time, or when heated, it gradually undergoes a change, yielding dipentene, a small amount of *d*-phellandrene, and an unknown lævorotatory terpene. This is the only case in which terpinolene has been found in a natural product.

The specific gravities, rotatory powers, refractive indices, and solubilities in 55% alcohol of some of the higher fractions have been determined. In most cases these fractions were inactive or slightly lævorotatory. In one case only was a strongly dextrorotatory fraction, a_D^{30} + 71·6°, obtained. This fraction gave analytical results agreeing with the formula $C_{15}H_{26}O$, and when rubbed with a glass-rod, solidified. It is probably a sesquiterpene alcohol. Factors which affect the composition of the oils obtained from the resins are: (1) age of the resin; (2) temperature of distillation, and (3) time occupied in distilling. The two latter factors affect the yields of higher oil more than of the terpenes proper.

The optical activity of both *d*-limonene and of phellandrene decreases when the terpenes are kept, probably owing to oxidation. If dipentene is formed from *d*-limonene at high temperatures (compare Wallach, Abstr., 1885, 550), the change is extremely slow, and even at 380° it would take many hours for the formation of an amount sufficient for detection. Limonene is almost completely polymerised when heated on the water-bath with a little dilute sulphuric acid dissolved in glacial acetic acid. Boiling with a mixture of absolute alcohol and a little dilute sulphuric acid converts the terpene into a mixture of inactive terpenes with relatively high boiling points, 184—200°, whereas boiling with sulphuric acid in dilute alcohol produces hydration. The addition of hydrochloric acid to limonene and its subsequent removal by means of aniline transforms a considerable proportion of the limonene into dipentene. Limonene hydrochloride has b. p. 89—91°/12 mm. The phellandrene obtained from the different resins was Wallach's *a*-phellandrene. The nitrite after solution in ethyl acetate at 30° and crystallising at the temperature of a freezing mixture has m. p. 120—121°, but if crystallised from hot ethyl acetate it has the lower m. p. given by Wallach. The solution of the nitrite in chloroform gradually diminishes in activity, and after some four hours is inactive, but after a longer period may become dextrorotatory.

The hydrocarbon is not racemised when heated at 200° for ten hours in a sealed tube, but at 225—250° the phellandrene is decomposed. It forms a hydrochloride which decomposes when distilled under reduced pressure. The dibromide is a mobile oil. When kept for some time, phellandrene is oxidised by the atmospheric oxygen, yielding a crystalline compound, $C_{10}H_{18}O_2$, *dihydroxyphellandrene*, which separates from hot ethyl acetate in colourless needles, m. p. 164·5—165·5°.

J. J. S.

Volatile Oil of Juniperus Phœnicea. J. RODIÉ (*Bull. Soc. chim.*, 1907, [iv], 1, 492—497. Compare Abstr., 1906, i, 971. Bennett and Umney, *Pharm. J.*, **75**, 827).—The portion of this oil boiling above 180° contains a minute quantity of an aldehyde and 25·17% of alcohols calculated as $C_{10}H_{18}O$, of which 5·03% occurs in the form of esters. The *aldehyde*, isolated by means of its crystalline *compound* with sodium hydrogen sulphite, furnishes a liquid *oxime* and a corresponding *naphthacinchonic acid*, which is crystalline and decomposes at 275—276°. On oxidation with alkaline permanganate the aldehyde appears to be completely decomposed. It does not seem to be identical with any of the aldehydes known to occur in volatile oils.

The more volatile portion of the mixture of acids obtained by saponifying the esters contained in the non-terpenic portion of the oil include acetic and hexoic acids, and in addition probably a minute quantity of a second acid soluble in water. Two other acid fractions were obtained, the one boiling at 210—255° and the other at 255—265°; the latter is near the boiling point of decoic acid, but the material differs from this in specific gravity, and may be a mixture of a fatty with a hydroxy-acid, or is possibly identical with the acid which Fromm (Abstr., 1900, i, 402) obtained from German savin.

T. A. H.

Resin-balsam of Pinus halepensis. ALEXANDER TSCHIRCH and H. SCHULZ (*Arch. Pharm.*, 1907, **245**, 156—163).—This resin is used in Greece for preserving and flavouring wine; the sample examined had approximately acid number 130 and saponification number 150. From a solution of it in ether, 1% aqueous ammonium carbonate extracts *halepopinic acid*, $C_{21}H_{32}O_3$; this is amorphous, with m. p. 72°, acid number 171 (corresponding with monobasicity), and saponification number 217; its lead salt is soluble in alcohol.

From the remaining ethereal solution, 1% aqueous sodium carbonate solution extracted a crude acid, which yielded lead salts respectively insoluble and soluble in alcohol. The acid of which the lead salt is insoluble in alcohol, *halepopinolic acid*, $C_{17}H_{26}O_2$, is crystalline, has m. p. 148—149°, acid number 187 (corresponding with monobasicity), and saponification number 246; its *silver* salt was analysed. This acid can be isolated from the balsam in several different ways. The acid of which the lead salt is soluble in alcohol, *halepopinitolic acid*, $C_{16}H_{26}O_2$, is amorphous, and has m. p. 78—80°, acid number 188 (corresponding with monobasicity), and saponification number 247.

From the remaining ethereal solution the ether was distilled off, and the residue was distilled with steam. An *essential oil* passed over, with b. p. 150—152°, and D 0·897, whilst a small quantity of a *resen* remained behind.

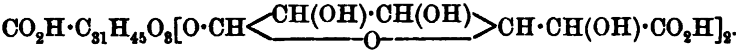
The balsam also contains a *bitter principle* in small amount.

In one hundred parts of the resin there are contained approximately: halepopinic acid, 5; halepopinolic and halepopinitolic acids, 59;

essential oil, 21—26; resen, 0·6; the residue consists of impurities mechanically mixed with the balsam. C. F. B.

Glycyrrhizin. ALEXANDER TSCHIRCH and H. CEDERBERG (*Arch. Pharm.*, 1907, **245**, 97—111).—Glycyrrhizin consists of the potassium and calcium salts of glycyrrhizic acid and was isolated from liquorice.

Glycyrrhizic acid, $C_{44}H_{64}O_{19}$, m. p. 205°, does not contain nitrogen, has a sweet taste, and is optically inactive. Its acid number corresponds with tribasicity; the mono-*potassium* and mono-*ammonium* salts, obtained by crystallisation from acetic acid, were analysed. The acid forms a *hexa-acetyl* derivative, with m. p. 210°. It does not reduce ammoniacal silver solution or Fehling's solution. When fused with potassium hydroxide, it yields acetic and oxalic acids, but no protocatechuic or *p*-hydroxybenzoic acid. When it is boiled for five hours with 3% sulphuric acid, air being excluded, *glycyrrhetic acid*, $C_{32}H_{48}O_7$ (molecular weight determined ebullioscopically), m. p. 210° (hitherto known as "glycyrrhetin"), is precipitated, and can be crystallised from acetic acid; this has an acid number corresponding with monobasicity, and forms a *diacetyl* derivative with m. p. 219°. The solution from which this acid has separated contains glycuronic acid, which has not been obtained hitherto from a vegetable source. The behaviour of glycyrrhizic acid is thus in harmony with the formula



$$CO_2H\cdot C_{31}H_{45}O_8[O\cdot CH<\underset{\text{——————}O\text{——————}}{CH(OH)\cdot CH(OH)}>CH\cdot CH(OH)\cdot CO_2H]_2.$$

Glycyrrhizic Acid.

The drug contains about 3% of glycyrrhizic acid, also 0·2% of a fatty *substance* with a bitter taste, and dextrose. Mannitol is present in the liquid from which the crude glycyrrhizic acid has been precipitated with sulphuric acid, but it is not present in the original drug. C. F. B.

Jafferabad and Uganda Aloes. EUGÈNE LÉGER (*J. Pharm. Chim.*, 1907, **25**, [vi], 476—483. Compare Abstr., 1900, i, 512; 1902, i, 549, 685, ii, 484; 1903, i, 356; 1904, i, 907).—Jafferabad aloes, derived from *Aloe abyssinica*, contains barbaloin, identical with that present in Barbadoes aloes (compare Shenstone, *Pharm. J.*, **13**, 461, and Tschirch and Hoffbauer, Abstr., 1905, i, 913). Uganda aloes, probably derived like Cape aloes from *Aloe ferox*, also contains barbaloin (compare Naylor and Bryant, *Pharm. J.*, 1899, 296, and Tschirch and Klaveness, Abstr., 1901, i, 602). It is pointed out that as the melting points of the aloins are indefinite they are untrustworthy as means of identification. T. A. H.

Rottlerin. HERMANN THOMS (*Arch. Pharm.*, 1907, **245**, 154—155). —A reply to Telle (this vol., i, 435). C. F. B.

Action of Magnesium Phenyl Bromide on Caffeine, and some of its Derivatives. HEINRICH SCHULZE (*Ber.*, 1907, **40**, 1744—1754). —By the interaction of magnesium phenyl bromide and caffeine or bromocaffeine in benzene solution a *compound*, $C_{20}H_{20}ON_4$, is formed along with diphenyl and triphenyl carbinol. This separates in colourless, short, many-faced crystals, m. p. 249—250°, and is a monoacid base; the *hydrochloride* crystallises in long, colourless, silky needles, m. p. 250°; the *aurichloride* forms yellowish-red needles, m. p. 200—202° (decomp.); the *platinichloride*, brownish-yellow, glistening plates, decomposing about 183°.

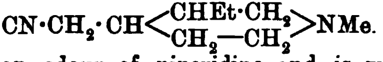
8-Methylcaffeine gives a *compound*, $C_{21}H_{22}ON_4$, m. p. 224—225°, crystallising in long, glistening needles; the *hydrochloride* forms colourless needles decomposing at 262—263°, and the *platinichloride*, brownish-yellow, glistening plates, m. p. 234° (decomp.). A considerable quantity of bases soluble in water is also produced during the above reactions.

Ethoxycaffeine yields a faintly basic *compound*, $C_{26}H_{24}ON_4$, m. p. 235°, crystallising in colourless, right-angled plates which dissolves in sulphuric acid with a red coloration; the *aurichloride* forms orange-red, glistening plates, m. p. 215°, whilst the corresponding *platinichloride* forms orange plates, which darkens at 250°, m. p. 271—272°. This compound is also produced from methoxycaffeine; it is probably an homologue of the compounds $C_{20}H_{20}ON_4$ and $C_{21}H_{22}ON_4$, in which the alkoxy-group has been replaced by phenyl.

In addition, a strongly basic *compound*, $C_{20}H_{22}N_4$, m. p. 152—153°, crystallising in bright, yellow, long needles is formed either from ethoxy- or methoxy-caffeine. The *hydrochloride* crystallises in yellow needles, which become fiery red on heating, m. p. 224° (decomp.); it dissolves in water with a reddish-yellow coloration.

Ethoxycaffeine yields a third faintly basic substance, sparingly soluble in water, crystallising in long, colourless, silky needles, which darkens about 200°, m. p. 255° (decomp.). Methoxycaffeine does not yield a similar product. E. F. A.

Derivatives of Cincholeupone. I. Paul Rabe [and Ernst Ackermann] (*Ber.*, 1907, **40**, 2013—2015. Compare Rabe, this vol., i, 78; Königs, Bernhart, and Ibele, this vol., i, 345).—*iso*Nitrosomethylcinchotoxine (Rohde and Schwab, Abstr., 1905, i, 228) when treated with phosphorus pentachloride and then poured into ice-cold water, yields cinchonic acid and the *nitrile* of methylcincholeupone,



$$CN\cdot CH_2\cdot CH<\begin{matrix}CHEt\cdot CH_2\\ CH_2—CH_2\end{matrix}>NMe.$$

The latter is a clear liquid with an odour of piperidine and is moderately soluble in water; b. p. 186—187°/90—95 mm., D_4^{20} 0·9366, n_D^{20} 1·4707. The *methiodide*, $C_{11}H_{21}N_2I$, form prismatic needles, decomposing at about 270°. The *picrate*, $C_{16}H_{22}O_7N_5$, crystallises in lemon-yellow plates, m. p. 142°, and the *picrolonate*, $C_{20}H_{26}O_5N_6$, in rhombic, pale orange-coloured plates, m. p. 208°. J. J. S.

Action of Nitric Acid on Cinchonine. Paul Rabe and Ernst Ackermann (*Ber.*, 1907, **40**, 2016—2017. Compare Weidel, *Annalen*, 1874, **173**, 76).—A diacid *base*, $C_{19}H_{20}O_6N_4$, has been obtained by heating cinchonine with nitric acid (D 1·3) in an oil-bath at 100—110° for some forty-eight hours. It is isolated by pouring into ice-cold water and adding a slight excess of ammonia. It crystallises from alcohol in slender needles, m. p. 238° (decomp.), is insoluble in ether or light petroleum and only sparingly soluble in benzene, chloroform, or alcohol. The *hydrochloride*, $C_{19}H_{20}O_6N_4,2HCl$, decomposes at 238°. The base is stable towards permanganate, but is oxidised by chromic acid to cinchonic acid. J. J. S.

Constitution of Morphine and of Hydroxymethylmorphimethine. Robert Pschorr and Hans Einbeck (*Ber.*, 1907, **40**, 1980—1983).—A reply to Knorr and Hörlein (Abstr., 1906, i, 877). Hydroxymethylmorphimethine (Knorr and Schneider, Abstr., 1906, i, 449) reacts not only as an alcohol, but also as a ketone. The *semicarbazone*, $C_{20}H_{26}O_4N_4$, m. p. 155°, crystallises from ethyl acetate in glistening plates containing the solvent. The *oxime* is not crystalline; its *hydrochloride*, $C_{19}H_{25}O_4N_2Cl$, decomp. 279° (corr.). Neither hydroxycodeine (Ach and Knorr, Abstr., 1903, i, 849) nor α- or β-methylmorphimethine give semicarbazones or oximes and the conclusion is drawn that the bridge of the phenanthrene nucleus is dihydrogenised in hydroxycodeine, but unsaturated in hydroxymethylmorphimethine, and (in opposition to Knorr) that there is attached to it the nitrogen and not the carbon side-ring in hydroxycodeine and in the morphine alkaloids, thus providing a further support for Pschorr's pyridine formula for morphine. W. R.

Morphine. IX. *iso*Codeinone and the Isomerism of Codeine, *iso*Codeine, and ψ-Codeine. Ludwig Knorr and Heinrich Hörlein (*Ber.*, 1907, **40**, 2032—2039. Compare this vol., i, 151; Schryver and Lees, Trans., 1901, **79**, 576).—Codeine and ψ-codeine when oxidised carefully with chromic acid yield the same ketone, *iso*codeinone, isomeric with codeinone. When decomposed, this ketone yields a phenanthrene derivative isomeric with that obtained from codeinone. The conclusion drawn from these facts is that *iso*- and ψ-codeine are structurally identical and only stereoisomeric, whereas codeine and *iso*codeine are structurally isomeric. All three compounds yield the same deoxycodeine (this vol., i, 235), and the isomerism is probably due to the different positions occupied by the hydroxyl group in the compounds, and the conversion of codeine into the isomeric bases is then accompanied by a wandering of the hydroxyl radicle.

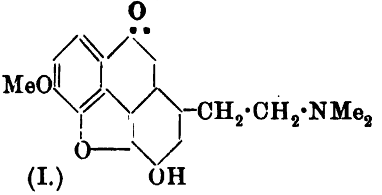
iso*Codeinone*, $C_{18}H_{19}O_3N$, may be isolated as its sparingly soluble chromate. It crystallises from alcohol in long, compact prisms, m. p. 174—175°, decomposes at 240°, $[\alpha]_D^{15}$ −25° in 99% alcohol. It does not give a characteristic reaction with sulphuric acid, and, unlike codeinone, is comparatively stable towards dilute hydrochloric acid. With concentrated hydrochloric acid, it yields phenolic bases. With acetic anhydride, it is decomposed, yielding methylethanolamine, but the main product is triacetylthebenine (Freund and Michaels, Abstr., 1897, i, 495).

iso*Codeinone-oxime*, $C_{18}H_{20}O_3N_2$, has been obtained in an amorphous condition only; the *semicarbazone*, $C_{19}H_{22}O_3N_4$, forms slender needles, m. p. 180° (decomp.), the corresponding *codeinone semicarbazone* has m. p. 185° (decomp.), and then solidifies and begins to decompose at about 250°. iso*Codeinone methiodide*, $C_{18}H_{19}O_3N,MeI$, crystallises in flat needles, which decompose at about 220°, $[\alpha]_D^{15}$ −12° in aqueous solution. It is more stable than codeinone methiodide and may be crystallised from water, but is decomposed by sodium hydroxide, yielding a *phenolic base*, $C_{19}H_{21}O_3N$, which decomposes at about 235°. When heated with alcohol at 160—170°, the methiodide yields a diacetoxymethoxyphenanthrene, m. p. 155—156°, which is isomeric with the product obtained from codeinone methiodide (Knorr, Abstr., 1904, i, 916) and dimethylaminoethyl ether, J. J. S.

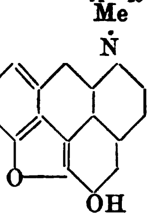
Morphine. X. 9-Amino-3 : 4-dimethoxyphenanthrene and 3 : 4-Dimethoxyphenanthrene-9-carboxylic Acid. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, **40**, 2040—2042).—The *ethyl* ester of dimethylmorphole-9-carboxylic acid, $C_{19}H_{18}O_4$ (Pschorr and Sumuleanu, Abstr., 1900, i, 487) form compact crystals, m. p. 80°. With hydrazine hydrate in absolute alcoholic solution, it yields the *hydrazide*, $C_{17}H_{16}O_3N_2$, m. p. 207—208°. The corresponding *azide*, $C_{17}H_{13}O_3N_3$, crystallises in pale yellow plates, decomposes at about 85°, and when heated with ethyl alcohol yields the *urethane* of 9-aminodimethylmorphole, $C_{19}H_{19}O_4N$, m. p. 145°. When hydrolysed with alcoholic potassium hydroxide, the urethrane yields 9-aminodimethylmorphole as an oil. The *hydrochloride* and *sulphate* are both sparingly soluble.

J. J. S.

Morphine. XI. Hydroxymethylmorphimethine (Ketodihydromethylmorphimethine). LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, **40**, 2042—2048).—The degradation of hydroxycodeine (Knorr and Schneider, Abstr., 1906, i, 449) is analogous to the toxin decomposition of quinine alkaloids or to the conversion of narcotine into narceine, and the compound described as hydroxymethylmorphimethine (*loc. cit.*) is now shown to be *ketodihydromethylmorphimethine* (I). With acetic anhydride it yields a mono- and not a diacetyl derivative. The following derivatives of the acetyl derivative have been prepared and analysed: *hydriodide*, $C_{21}H_{25}O_5N,HI$, m. p. 270° (decomp.); *hydrobromide*, quadratic plates, decomposing at 280—285°; methiodide (*loc. cit.*). Hydroxycodeine yields a diacetyl derivative (Ach and Knorr, Abstr., 1903, i, 849). It would thus appear that the oxygen atom introduced into the molecule of codeine in its oxidation to hydroxycodeine is present in this latter as a hydroxy-group, but is no longer present in this form in ketodihydromethylmorphimethine, but appears again as phenolic hydroxyl when the base is decomposed with aceticanhydride, yielding a phenanthrene derivative. The ketonic nature of ketodihydromethylmorphimethine has been proved by conversion into an oxime and semicarbazone. The *oxime* yields a crystalline *methiodide*, $C_{19}H_{24}O_4N_2,MeI$, which changes colour at 250° and decomposes rapidly at 270°.



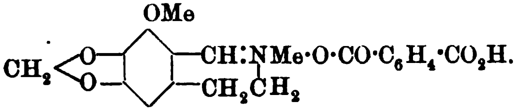
(I.)



(II.)

The annexed formula (II) is suggested for morphine. J. J. S.

Preparation of Acid and Normal Cotarine Phthalates. KNOLL and Co. (D.R.-P. 180395).—*Cotarnine hydrogen phthalate* is prepared by shaking or stirring together in absolute ether an intimate mixture of cotarnine and phthalic anhydride until the product is completely soluble in water. The reagents are employed in molecular proportion and when the amount of cotarnine is doubled the normal *cotarnine phthalate* is produced. G. T. M.



Application to Pyridine of the Direct Method of Hydrogenation by Means of Nickel. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, **144**, 784—786).—When pyridine vapour mixed with excess of hydrogen is passed over a column of reduced nickel kept at 160—180°, the product is found to contain a small quantity of an amine which is not piperidine, but is probably normal amylamine, it resembles *iso*amylamine in properties. If the nickel is heated at 220°, the amylamine formed breaks down into pentane and ammonia (compare Hoffmann Abstr., 1883, 813), at 350° the destruction of the pyridine is much more rapid. This rupture of the pyridine nucleus on attempted hydrogenation in presence of nickel has already been observed by Padoa and Carughi (Abstr., 1906, i, 765) in the case of quinoline, methyl-*o*-toluidine here being the final product. The fact that the benzene nucleus is readily hydrogenated by this method, whilst the pyridine ring is not, is evidence against the Körner formula for the latter substance. On passing piperidine vapour alone over reduced nickel heated at 250°, it is completely decomposed into pyridine and hydrogen. E. H.

Derivatives of Quinquevalent Chromium. III. RUDOLF F. WEINLAND and MAX FIEDERER (*Ber.*, 1907, **40**, 2090—2093. Compare this vol., ii, 31, and Weinland and Friedrich, Abstr., 1906, i, 37).—The pyridinium tetrachlorohydroxychromanate, $C_5NH_5,CrCl_4·OH$, previously described, is most conveniently prepared by saturating glacial acetic acid with hydrogen chloride, dissolving chromic acid in this, and after an interval adding pyridine dissolved in acetic acid. The salt crystallises without water in brownish-red, doubly refractive, right-angled plates. The quinolinium salt can be prepared in a similar manner; it also crystallises without water. The method is also available for preparing the alkali salts of the type $CrOCl_3,2KCl$.
E. F. A.

New Method of Introducing Alkyl or Aryl Groups into Pyridine or Quinoline Bases. Constitution of Mixed Organo-magnesium Compounds. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 538—545).—The author has continued the study of the compounds obtained by the action of mixed organo-magnesium compounds on the pyridine and quinoline bases (Abstr., 1904, i, 920; see also Sachs and Sachs, Abstr., 1904, i, 925; Tschelinzeff, Abstr., 1905, i, 40). The results obtained render it possible to determine the constitution of all the organo-magnesium compounds yet prepared, starting from the known constitutions of Grignard's compounds.

It is found that when magnesium, an alkyl or aromatic halogen compound, and traces of pyridine or quinoline are brought into contact in toluene, benzene, or light petroleum, a reaction begins, in some cases in the cold, but soon ceases and leaves most of the magnesium unchanged, even though a small quantity of iodine is added and the mixture heated for a long time in a reflux apparatus. Hence, pyridine and quinoline do not act catalytically as does dimethylaniline, the reaction only proceeding as far as the formation of substituted ammonium iodide. If, however, 1 mol. of the pyridine or quinoline is added per mol. of the halogen compound, all the magnesium disappears and the reaction is complete in a few minutes. With aliphatic halogen compounds, the reaction proceeds in presence of either toluene or benzene or light petroleum, but with halogen derivatives of the aromatic series it is necessary for the solvent to have a b. p. of at lowest about 80°. The organo-magnesium compounds thus formed are obtained as a fine powder or crystalline magma, and alter far more rapidly than those described previously (Abstr., 1904, i, 920). The latter, when treated with water, yield the hydrocarbon corresponding with the alkyl radicle and the free base, but the compounds now described give, under the action of water, the base with an alkyl radicle in the nucleus. Thus, from bromobenzene, quinoline, and magnesium in toluene solution, 2-phenylquinoline is obtained.

Similar results are obtained on attempting to prepare the mixed compound of pyridine and quinoline with magnesium phenyl bromide by adding 1 mol. of each base to 1 mol. of the organo-metallic compound prepared by Grignard's method.

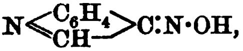
These compounds possess the structure $R\cdot Q\cdot Mg\cdot Alk$ (where $Q =$ quinoline or other base), whilst those previously described are represented by $R\cdot Mg\cdot Q\cdot Alk.$; these constitutions are indicated by the behaviour of the compounds towards water, a reaction which the author employs generally for determining the structure of mixed organo-magnesium compounds. In this way it is found that the constitutions of all the organo-magnesium compounds known are as follow. I. Oxonium type: (*a*) Grignard's mono-ether compounds, $R\cdot Mg\cdot OEt_2\cdot Alk.$; (*b*) Tschelinzeff's diether compound,

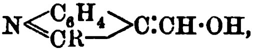
$$R\cdot Mg\cdot OEt_2\cdot OEt_2\cdot Alk.$$

(*loc. cit.*). II. Ammonium type, corresponding with the preceding in formula and in chemical behaviour: (*a*) Tschelinzeff's monodimethylaniline compound, $R\cdot Mg\cdot Q\cdot Alk.$; (*b*) monoquinoline compound of Sachs and Sachs (*loc. cit.*), $R\cdot Mg\cdot Q\cdot Alk.$; (*c*) polyquinoleic compounds of Oddo, $R\cdot Mg\cdot N(\vdots C_9H_7)\cdot NAlk.\vdots C_9H_7$ and

$$R\cdot Mg\cdot N(\vdots C_9H_7)\cdot N(\vdots C_9H_7)\cdot NAlk.\vdots C_9H_7.$$

III. Mixed oxonium-ammonium type: pyridine-ether compounds of Oddo, $R\cdot Mg\cdot N(\vdots C_5H_5)\cdot N(\vdots C_5H_5)\cdot OEt_2Alk.$, or with the ether molecule interchanged with one or other of the $N\vdots C_5H_5$ groups. All the above compounds, when treated with water, yield the hydrocarbons corresponding with the alkyl radicle of the haloid compound employed. IV. Ammonium type, isomeric with those of class II: (*a*) Oddo's compounds (Abstr., 1904, i, 920), $R{\cdot}Q{\cdot}Mg{\cdot}Alk.$; (*b*) compound obtained by Oddo by the simultaneous action of pyridine and quinoline on Grignard's compounds, $R{\cdot}N(:C_9H_7){\cdot}Mg{\cdot}NAlk.:C_5H_5$. The action of water on these compounds yields the alkylated bases. T. H. P.

Indoles. ANGELO ANGELI and GUERRIERO MARCHETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 381—384. Compare this vol., i, 436).—The action of nitrous acid on indole yields a compound,  $N{<}\genfrac{}{}{0pt}{}{C_6H_4}{CH}{>}C{:}N{\cdot}OH$, which is probably identical with the so-called nitrosoindole prepared by Zatti and Ferratini (Abstr., 1890, 1293; 1891, 67) by the action of sodium nitrite on an acetic acid solution of indole.

The action of formic acid on indoles, which should give rise to compounds of the form  $N{<}\genfrac{}{}{0pt}{}{C_6H_4}{CR}{>}C{:}CH{\cdot}OH$, yields, instead, compounds identical with those regarded as aldehydes,

$$NH{<}\genfrac{}{}{0pt}{}{C_6H_4}{CR}{>}C{\cdot}CHO.$$

On the other hand, ethyl formate generally yields hydroxymethylene derivatives. This explains why pyrrole-2-aldehyde (Bamberger and Djigerdjan, Abstr., 1900, i, 309), which exhibits behaviour only slightly resembling that of ordinary aldehydes, does not react with dihydroxyammonia (Abstr., 1905, ii, 385) to form the corresponding hydroxamic acid. Also the hydroxymethylene compounds,

$$R{\cdot}CO{\cdot}CH{:}CH{\cdot}OH,$$

which are formed by the action of ethyl formate on the ketones, $R{\cdot}CO{\cdot}CH_3$, and which were at first regarded as aldehydes,

$$R{\cdot}CO{\cdot}CH_2{\cdot}CHO,$$

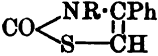
do not react with dihydroxyammonia, although they yield oximes, hydrazones, &c. The reaction with dihydroxyammonia is not given by 2-methylindole-3-aldehyde (Plancher and Ponti, this vol., i, 341), which, however, reacts readily with hydrazines and condenses with pyruvic acid and naphthylamines.

The authors term "true aldehydes," $R{\cdot}CHO$, and "nitroso-derivatives," $R{\cdot}NO$, the compounds which react with dihydroxyammonia, to distinguish them from hydroxymethylene compounds, $CHR{:}CH{\cdot}OH$, and oximes, $CHR{:}N{\cdot}OH$. In the case of true aldehydes, the formation of oximes and hydrazones takes place by addition of hydroxylamine or hydrazine to the double linking between carbon and oxygen: $R{\cdot}CH{:}O + NH_2{\cdot}OH = R{\cdot}CH(OH){\cdot}NH{\cdot}OH \longrightarrow R{\cdot}CH{:}N{\cdot}OH$, whilst, with hydroxymethylene compounds, the addition as to the double linking between 2 carbon atoms: $CHR{:}CH{\cdot}OH + NH_2{\cdot}OH =$

$$CH_2R{\cdot}CH(OH){\cdot}NH{\cdot}OH \longrightarrow CH_2R{\cdot}CH{:}N{\cdot}OH.$$

T. H. P.

Action of Bromoacetophenone on Thiocarbimides and Thiourethanes. REINHOLD VON WALTHER and H. GREIFENHAGEN (*J. pr. Chem.*, 1907, [ii], 75, 201—211. Compare this vol., i, 349; Völtzkow, Abstr., 1881, 43).—The stability of the condensation products of *s*-diphenyl- and *s*-ditolyl-thiocarbamides with bromoacetophenone

towards hydrochloric acid rendered attempts to prepare **oxythiazolines**, 

$\mathrm{CO}\!<\!\begin{array}{l}\mathrm{NR\cdot CPh}\\ \qquad\|\\ \mathrm{S—CH}\end{array}$

, by hydrolysis of the arylimino-group, unsuccessful. It is found now that such oxythiazolines are formed when phenyl- or *p*-tolyl-thiocarbimide is heated with bromoacetophenone in alcoholic, but not in benzene, solution under pressure at 110°. The condensation takes place in three stages: the thiourethane, $NHR\cdot CS\cdot OEt$, formed in the first stage, reacts with the bromoacetophenone, forming ethyl bromide and the intermediate product, $NHR\cdot CO\cdot S\cdot CH_2Bz$, which undergoes ring condensation with loss of water. Oxythiazolines cannot be obtained from *o*- or *m*-tolylthiocarbimide, but are formed by the action of bromoacetophenone on phenyl-, *o*- *m*-, or *p*-tolyl-thiourethane in boiling alcoholic solution, the ring condensation being completed on prolonged boiling with glacial acetic acid. The intermediate substance, $NHR\cdot CO\cdot S\cdot CH_2Bz$, can be isolated only from the product of the action of bromoacetophenone on *o*-tolylthiourethane.

2-*Oxy*-3 : 4-*diphenyl*-2 : 3-*thiazoline* crystallises in small prisms, m. p. 124°, and has feeble basic properties.

Tolylthiocarbimides are formed in 80% yields by boiling *s*-ditolylthiocarbamides with acetic anhydride.

2-*Oxy*-4-*phenyl*-3-p-*tolyl*-2 : 3-*thiazoline*, $R = C_7H_7$, crystallises from alcohol in needles, m. p. 130·5°.

2-*Oxy*-4-*phenyl*-3-m-*tolyl*-2 : 3-*thiazoline* crystallises in needles, m. p. 123°, dissolves in concentrated acids, and is reprecipitated by dilution with water.

The *compound*, $o\text{-}C_7H_7\cdot NH\cdot CO\cdot S\cdot CH_2\cdot COPh$, crystallises from alcohol in slender needles, m. p. 138°, dissolves in aqueous sodium hydroxide, forming a yellow solution, which has an odour of acetophenone, and yields a flocculent precipitate and an odour of hydrogen sulphide on addition of dilute sulphuric acid, and is converted slowly by cold concentrated sulphuric acid into 2-*oxy*-4-*phenyl*-3-o-*tolyl*-2 : 3-*thiazoline*. This separates from glacial acetic acid in stout crystals, m. p. 109°, dissolves in concentrated acids, and when heated with concentrated sulphuric acid yields *o*-toluidine sulphate.

G. Y.

Triphenylhydrazine. MAX BUSCH and RICHARD HOBEIN (*Ber.*, 1907, **40**, 2099—2102).—*Triphenylhydrazine*, $NPh_2\cdot NHPh$, prepared by the interaction of magnesium phenyl bromide with phenylhydroxylamine, crystallises in colourless needles which turn brown at 139°, m. p. 142°. It shows no basic properties and dissolves in anhydrous sulphuric or acetic acids with a yellow coloration which changes to violet. The *nitrosoamine*, $NPh_2\cdot NPh\cdot NO$, forms reddish-brown needles, m. p. 115°. When cautiously treated with ethereal hydrogen chloride, a more or less green, crystalline, rearrangement product is formed, the *hydrochloride* of 4-*amino*-4′-*anilinodiphenyl*,

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NHPh,$$

m. p. 136—137°. This dissolves in concentrated sulphuric acid with a violet-red coloration, and is coloured intensely violet-red by a trace of nitrate or nitrite.

p-Chlorophenylhydroxylamine and magnesium phenyl bromide under similar conditions yield *p*:*p'*-dichloroazobenzene, $C_6H_4Cl \cdot N \colon N \cdot C_6H_4Cl$, m. p. 184°, crystallising in silky, glistening, yellow needles.

E. F. A.

Additive Products of Trinitrobenzene Derivatives with Certain Aromatic Nitrogen Compounds. III. ROBERTO CIUSA and C. AGOSTINELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 409—412. Compare Abstr., 1906, i, 891, 962).—The authors describe further additive products, including several formed from picryl chloride and phenylhydrazones of aromatic aldehydes. These compounds are sparingly soluble in ordinary solvents and, like the corresponding trinitrobenzene, trinitrotoluene, and trinitrophenol derivatives, exhibit variations in colour and solubility related to the different radicles present in the benzene nuclei of the original aldehydes. That these radicles influence also the stability of the additive products is seen from the facts that the phenylhydrazones of benzaldehyde, *m*-nitrobenzaldehyde, and anisaldehyde yield compounds with *m*-dinitrobenzene which exist in solution, but could not be isolated, whilst piperonaldehydephenylhydrazone gives a well crystallised, additive compound with *m*-dinitrobenzene. These results are related to the observation that *iso*safrole and *iso*apiole, which contain the dioxymethylene group, give more stable picrates than *iso*methyleugenol and asarone, which contain only methoxy-groups.

The conclusion is drawn that the phenylhydrazones exhibit behaviour analogous to that of the secondary amines. If derived from aliphatic aldehydes or ketones, they have a marked basic character and yield yellow picrates, whilst those derived from aromatic aldehydes exhibit no basic character and give intensely-coloured picrates, and trinitrobenzene and trinitrotoluene derivatives. Similarly, aliphatic secondary amines yield yellow picrates, whilst diphenylamine, the indoles and carbazole give intensely-coloured, additive products with aromatic polynitrohydrocarbon derivatives.

Benzaldehydephenylhydrazone and picryl chloride give the *compound*, $C_{13}H_{12}N_2,2C_6H_2O_6N_3Cl$, which crystallises from alcohol in dark maroon, shining needles, m. p. 90—91°.

Piperonaldehydephenylhydrazone and picryl chloride give the *compound*, $C_{14}H_{12}O_2N_2,2C_6H_2O_6N_3Cl$, crystallising from alcohol in almost black, shining needles, m. p. 123°.

Piperonaldehydephenylhydrazone and *m*-dinitrobenzene yields the *compound*, $C_{14}H_{12}O_2N_2,C_6H_4(NO_2)_2$, which forms dark red, rhombic prisms, m. p. 73—74°.

Anisaldehydephenylhydrazone and picryl chloride give the *compound*, $C_{14}H_{14}ON_2,2C_6H_2O_6N_3Cl$, crystallising in shining, black, flattened needles, m. p. 92°.

m-Nitrobenzaldehydephenylhydrazone and picryl chloride yield the *compound*, $C_{13}H_{11}O_2N_3,2C_6H_2O_6N_3Cl$, which forms shining, brick-red needles, m. p. 105°.

Cinnamaldehydephenylhydrazone and picryl chloride give the *compound*, $C_{15}H_{14}N_2,2C_6H_2O_6N_3Cl$, which separates in minute, brick-red needles, m. p. 112—113°, sparingly soluble in alcohol.

2-Methylindole and picryl chloride yield the *compound*,

$C_9H_9N,2C_6H_2O_6N_3Cl$,

crystallising from alcohol in long, dark red needles, m. p. 115—116°.

3-Methylindole and picryl chloride give the *compound*,

$C_9H_9N,2C_6H_2O_6N_3Cl$,

which forms long, dark red needles, m. p. 112—113°. T. H. P.

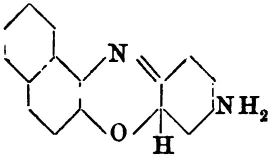
Conversion of Quinonephenylhydrazones into Hydroxyazo-compounds. KARL AUWERS (*Ber.*, 1907, 40, 2154—2159).—In a preliminary notice the author states briefly his reasons for regarding the acyl derivatives of hydroxyazo-compounds, excluding McPherson's quinonoid isomerides of the para series, as *O*-esters. Benzeneazo-*p*-cresol acetate and its hydrazo-compound are represented by

$N_2Ph{\cdot}C_6H_3Me{\cdot}OAc$ and $NAcPh{\cdot}NH{\cdot}C_6H_3Me{\cdot}OH$.

The latter should yield by careful oxidation the quinonoid *N*-acetate, $NAcPh{\cdot}N{:}C_6H_3Me{:}O$, but in all cases the ordinary, yellow *O*-ester is obtained.

The benzoylation of β-benzeneazo-α-naphthol in pyridine produces a dark red benzoate, which is apparently different from McPherson's yellow benzoate obtained from β-naphthaquinone and α-benzoylphenylhydrazine, but the two substances are shown to be identical by the method of mixed melting point, by their chemical transpositions, and by their crystallographic properties; the benzoate must be an *O*-ester, since it yields a hydrazo-compound by reduction. Similar results are recorded in the case of β-benzeneazo-α-naphthol acetate. In connexion with the wandering of the acetyl group which must take place during the change of the quinonoid structure into the benzene nucleus, the author quotes his experiments on *p*-alkylidenedihydrobenzenes (this vol., i, 399). C. S.

Azoxonium Compounds. V. Azoxonium Compounds derived from β-Naphthaquinone. FRIEDRICH KEHRMANN, H. DE GOTTRAU, and G. LEEMANN (*Ber.*, 1907, 40, 2071—2089).—The Nietzki-Otto dye (Abstr., 1888, 949) produced by condensation of quinonedichloroimide with β-naphthol contains an amide group, since in acid solution, on heating, the azo-group is removed and salts of naphthaphenazoxonium are formed. These are immediately further oxidised in the naphthalene nucleus, forming 3-aminophenonaphthazoxone. Similarly, the Nietzki-Otto compound, when ground with aniline, left exposed to the air for twenty-four hours, and treated with alcohol, gives rise to a metallic green powder and a violet filtrate; the former is *3-amino-6-anilinonaphthaphenazoxonium*, whilst the violet dye contains the anilino-group substituted in the benzene nucleus; the *leuco*-compound (annexed formula) crystallises as *hydrochloride* in bright yellow needles and forms an *acetyl* derivative of which the brownish-yellow crystals decompose at 210° and give a yellow, fluorescent solution. On oxidation with ferric chloride a reddish-violet coloration is produced which changes to purple-red and gives a dark red precipitate with sodium chloride



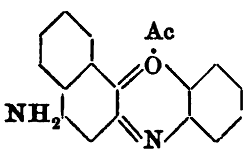
solution which slowly decolorises in water. The salts at first formed are unstable and oxidise to acetaminophenonaphthazoxone.

4-Amino-1 : 2-naphthaquinone and *o*-aminophenol condense in acid solution to a *compound*, $C_{16}H_{12}ON_2$, isomeric with the Nietzki dye, which is citron-yellow coloured and a pronounced base. Condensation in acetic acid solution leads to the production of the *acetate*. The *nitrate* forms dark brown, metallic, glistening needles; the *platinichloride* is a brownish-red, crystalline powder, and the *dichromate* a bright red. The *base* gives an *anhydride* crystallising in straw-yellow, glistening needles, m. p. 215°. Nitrous acid is quite without action on the base. The *acetate* crystallises in orange-yellow, glistening needles, m. p. 193—194°, and forms magenta-red salts of undoubtable azoxonium constitution, whereas the base itself and its orange-red salts are true *p*-quinoneimide derivatives. *o*-Amino-*m*-cresol yields a similar red dye, forming a red *platinichloride* and orange-yellow *acetate*, decomposing at 170—180°.

4-Acetylamino-β-naphthaquinone condense to a *pseudo-base*,

$$C_{18}H_{14}O_3N_2,$$

decomposing at 160—170°, of which the greenish-yellow crystals give a reddish-violet coloration in concentrated sulphuric acid. The *chloride* is red and can also be prepared by direct condensation with *o*-aminophenol hydrochloride.

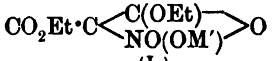


9-*Aminoisonaphthaphenazoxonium* salts :—the *methylate* of the *pseudo-base*, $C_{17}H_{14}O_2N_2$, forms sulphur-yellow needles, m. p. 170° (decomp.), which dissolve in sulphuric acid with a magenta-red coloration; the *chloride* forms blackish-violet crystals and the *platinichloride* glistening, violet needles. The chloride gives a blood-red solution in warm water, which, on evaporation, yields violet and yellow crystals, the former corresponding with the oxonium and the latter with the quinoneimide formula. The *pseudo-base*, $C_{19}H_{16}O_3N_2$, obtained in a similar manner from *o*-amino-*m*-cresol and acetylaminonaphthaquinone, decomposes at 170—180°, dissolves in sulphuric acid with a bluish-violet coloration, and forms orange-red oxonium salts. The *pseudo-base* of 9-*amino*-2-*methylisonaphthaphenazoxonium* decomposes at 160° and behaves similarly to the lower homologue. E. F. A.

Colourless, Yellow, and Red Salts of Nitro-ketones. ARTHUR HANTZSCH [and, in part, A. SALWAY] (*Ber.*, 1907, **40**, 1523—1532; compare this vol., i, 500, 513).—The salt-forming nitro-ketones containing the group $\cdot CO \cdot CH(NO_2) \cdot$ are closely related to the *o*-nitrophenols, the grouping $\cdot C(OH) \colon C(NO_2) \cdot$, formed in the case of the former by enolisation, being present in both classes. In agreement with this is the formation by nitro-ketones of red and yellow salts; more important, however, is the formation of colourless salts, unknown in the case of the nitrophenols, which shows that, contrary to Kauffmann's view, a metallic atom or the group $\cdot OM'$ has no auxochromic properties.

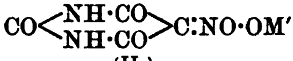
Of the substances containing the grouping $\cdot CO \cdot CH(NO_2) \cdot$ which have been investigated, nitromalonamide, having the affinity constant

$K = 0{\cdot}058$, forms with colourless metallic ions, colourless salts yielding colourless solutions. Ethyl nitromalonate, $K = 0{\cdot}073$, forms colourless salts, $OM'{\cdot}NO{:}C(CO_2Et)_2$, which are yellow in aqueous solution when the structure of the ion may correspond to the salt (I). The monometallic salts of nitrobarbituric acid are colourless when solid, but yellow in aqueous solution; the solid salts are considered to have the structure (II), but the yellow ion the structure (III).



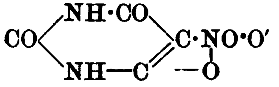
$CO_2Et{\cdot}C<\begin{matrix}C(OEt)\\NO(OM')\end{matrix}>O$

(I.)



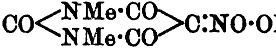
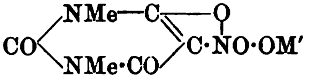
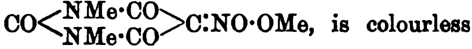
$CO<\begin{matrix}NH{\cdot}CO\\NH{\cdot}CO\end{matrix}>C{:}NO{\cdot}OM'$

(II.)



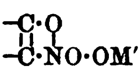
(III.)

The di- and tri-metallic salts of nitrobarbituric acid, which are yellow, must be derived from the coloured ion.

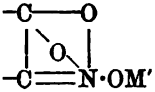
Contrary to statements in the literature, nitrodimethylbarbituric acid, when free from dimethylvioluric acid, yields only two series of salts: colourless salts,  $CO<\begin{matrix}NMe{\cdot}CO\\NMe{\cdot}CO\end{matrix}>C{:}NO{\cdot}OM'$ ($M' = NH_4$ or Ag), and yellow salts,  ($M' = $ Li, Na, K, Rb, Cs, or $NPhMe_3$); the aqueous solutions are yellow, whilst the *aci*-ether,  $CO<\begin{matrix}NMe{\cdot}CO\\NMe{\cdot}CO\end{matrix}>C{:}NO{\cdot}OMe$, is colourless.

4-Nitro-1-phenyl-3-methylpyrazolone forms yellow *lithium*, *ammonium*, and *trimethylammonium* salts which crystallise with 1 mol. of water of crystallisation; the yellow sodium salt (H_2O) is formed in aqueous solution, or anhydrous by the action of sodium ethoxide on the nitropyrazolone in benzene solution; when boiled with toluene it is converted into a red, anhydrous salt. The *potassium* salt (H_2O) is yellow, loses H_2O at 135° without change of colour, but at 150° is converted into the red, anhydrous salt. The anhydrous *silver* and *mercurous* salts are colourless.

In the discussion of these experimental results, it is noted that the formation of yellow solutions from colourless salts is at variance with the view previously put forward that colour does not appear on simple ionisation. The formation of coloured salts cannot depend on the extent of the isomerisation of the enolic nitro-ketone, since the nitropyrazolone, which is only a feeble acid, behaves similarly to the strongly acid nitrodimethylbarbituric acid, neither can the colour be connected with the presence or absence of water of crystallisation. The nature of the "colourless" metallic ion has a certain influence, since the strongly positive alkali metals have more tendency to the formation of coloured salts than the more feebly positive ammonium, silver, or mercury; on the other hand, the tendency to the formation of the red salt of the nitropyrazolone is more pronounced with sodium than with the more positive of the alkali metals.

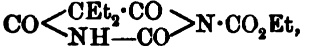


(IV.)



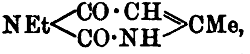
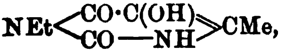
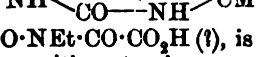
(V.)

It is argued that the colourless (*leuco*-) salts and ethers are derivatives of the *aci*-nitro-ketones containing the group –CO·C(NO·OH)–, whilst the coloured (*chromo*-) salts contain the grouping (IV); the yellow and red salts are possibly *syn*- and *anti*-stereoisomerides, but may be structural isomerides, one containing the preceding grouping, the other the grouping (V). G. Y

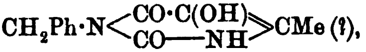
[Carbalkyloxy-5 : 5-dialkylbarbituric Acids.] WILHELM TRAUBE (D.R.-P. 180424).—In the condensation of dialkylmalonyl chlorides with urethanes the main product is a dialkylmalonylurethane, but a further decomposition occurs to some extent, leading to the formation of a carbalkyloxydialkylbarbituric acid. Thus diethylmalonyl chloride and urethane when heated for some time in boiling xylene yield principally diethylmalonyldiurethane, but carbethoxydiethylmalonide and *carbethoxydiethylbarbituric acid*, m. p. 60—65°,  $CO{<}\genfrac{}{}{0pt}{}{CEt_2\cdot CO}{NH—CO}{>}N\cdot CO_2Et$, are also produced.

The latter which is isolated by distillation under reduced pressure is converted into diethylbarbituric acid by the action of either fuming sulphuric acid or alkaline agents such as sodium ethoxide.

Carbethoxydipropylbarbituric acid is similarly prepared, but has not been obtained crystalline; it is readily converted into dipropylbarbituric acid. G. T. M.

Alkyl Derivatives of Methyluracil. OTTO HOEBEL (*Annalen*, 1907, **353**, 242—266. Compare Behrend and Dietrich, Abstr., 1900, i, 120; Behrend and Thurm, Abstr., 1902, i, 832).—It was shown by Behrend and Fricke (Abstr., 1903, i, 739) that hydroxy-1 : 4-dimethyluracil is obtained on oxidation of trimethyluracil by means of potassium permanganate, and by Behrend and Hufschmidt (Abstr., 1906, i, 310) that whilst on oxidation 1 : 4-dimethyluracil yields hydroxy-1 : 4-dimethyluracil, 3 : 4-dimethyluracil is oxidised to hydroxy-4-methyluracil. This difference in the stability towards oxidising agents of alkyl groups in positions 1 and 3 in uracil has been studied now in the case of ethyl and benzyl derivatives of 4-methyluracil. It is found that whilst 4-methyl-1-ethyluracil,  $NEt{<}\genfrac{}{}{0pt}{}{CO\cdot CH}{CO\cdot NH}{>}CMe$, on oxidation in acetic acid solution with potassium permanganate, equivalent to two atoms of oxygen, yields hydroxy-4-methyl-1-ethyluracil,  $NEt{<}\genfrac{}{}{0pt}{}{CO\cdot C(OH)}{CO—NH}{>}CMe$, under the same conditions 4-methyl-3-ethyluracil, $NH{<}\genfrac{}{}{0pt}{}{CO—CH}{CO\cdot NEt}{>}CMe$, yields acetaldehyde, hydroxy-4-methyluracil,  $NH{<}\genfrac{}{}{0pt}{}{CO\cdot C(OH)}{CO—NH}{>}CMe$, and oxaluric acid. Ethyloxaluric acid, $NH_2\cdot CO\cdot NEt\cdot CO\cdot CO_2H$ (?), is formed from both methylethyluracils on oxidation with potassium permanganate equivalent to three atoms of oxygen in alkaline solution, but together with acetylethylcarbamide, NHEt·CO·NHAc, from 4-methyl-1-ethyluracil only.

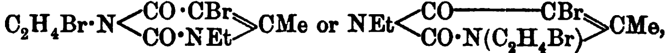
The benzyl groups of 1-benzyl- and 3-benzyl-4-methyluracils undergo oxidation more easily than the ethyl groups of the above methylethyluracils, since both benzyl compounds yield considerable amounts of benzaldehyde and benzoic acid. The 1-benzyl compound is more stable than its isomeride, since it yields hydroxybenzylmethyluracil,



$CH_2Ph\cdot N<\begin{array}{l}CO\cdot C(OH)\\ CO—NH\end{array}>CMe$ (?), together with traces of oxaluric acid, whilst much oxaluric acid, but no hydroxybenzylmethyluracil, is obtained on oxidation of the 3-benzyl compound. Both benzyl compounds yield also the same benzyloxaluric acid, but no acetylbenzylcarbamide.

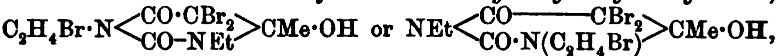
The action of ethyl bromide on potassium 4-methyluracil in alcoholic solution on the water-bath leads to the formation of two isomeric ethyl derivatives (compare Hoffmann, Abstr., 1890, 31). 4-Methyl-3-ethyluracil crystallises from absolute alcohol in needles, m. p. 195°, and on methylation yields 1 : 4-dimethyl-3-ethyluracil, m. p. 110° (Behrend and Thurm, *loc. cit.*). 4-Methyl-1-ethyluracil crystallises from water in microscopic needles, m. p. 195°, is soluble in alcohol, and on methylation yields 3 : 4-dimethyl-1-ethyluracil, m. p. 111·5—113·5° (Behrend and Thurm, *loc. cit.*). A mixture of the two methylethyluracils has m. p. 160—165°.

4-Methyl-1 : 3-diethyluracil (Hoffmann, *loc. cit.*), which is formed together with the monoethyl compounds, reacts with bromine in presence of water, forming *dibromomethyldiethyluracil*,



$$C_2H_4Br\cdot N<\begin{array}{l}CO\cdot CBr\\ CO\cdot NEt\end{array}>CMe \text{ or } NEt<\begin{array}{l}CO—CBr\\ CO\cdot N(C_2H_4Br)\end{array}>CMe,$$

which crystallises in octahedra, m. p. 121—122°, and on treatment with an excess of bromine yields *tribromohydroxymethyldiethyluracil*,



$$C_2H_4Br\cdot N<\begin{array}{l}CO\cdot CBr_2\\ CO—NEt\end{array}>CMe\cdot OH \text{ or } NEt<\begin{array}{l}CO—CBr_2\\ CO\cdot N(C_2H_4Br)\end{array}>CMe\cdot OH,$$

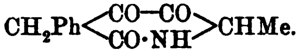
m. p. 94—97° ; this is reconverted into the dibromo-compound on prolonged boiling with absolute alcohol.

The action of benzyl chloride on potassium methyluracil in alcoholic solution on the water-bath leads to the formation of a mixture of benzylmethyluracils, of which the more sparingly soluble in alcohol is 3-*benzyl*-4-*methyluracil*, crystallising in microscopic, hexagonal leaflets, m. p. 232—233°. On methylation this yields 3-*benzyl*-1 : 4-*dimethyluracil*, crystallising in hexagonal leaflets, m. p. 82°.

1-*Benzyl*-4-*methyluracil* crystallises from alcohol in microscopic, rectangular leaflets, m. p. 174—177°, and on methylation yields 1-*benzyl*-3 : 4-*dimethyluracil*, long needles, m. p. 159—161°, which is formed also by benzylation of 3 : 4-dimethyluracil.

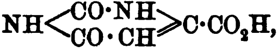
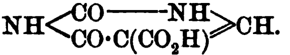
Hydroxy-4-*methyl*-1-*ethyluracil* decomposes at 230°, gives a blue coloration with ferric chloride, and forms an *acetyl* derivative, $C_9H_{12}O_4N_2$, which crystallises in needles, m. p. 189°.

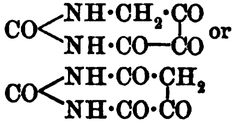
Ethyloxaluric acid, $C_5H_8O_4N_2$, crystallises in glistening leaflets, decomposes at 167—169°, and gives the characteristic reaction for oxaluric acids with ammonia and calcium chloride (compare Behrend and Grünewald, Abstr., 1902, i, 834).

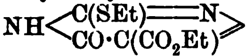
Hydroxy-1-*benzyl*-4-*methyluracil* crystallises from methyl alcohol in leaflets and commences to decompose at 220°; as it does not give a blue coloration with ferric chloride, it may have the ketonic constitution  $\mathrm{CH_2Ph}<\begin{matrix}\mathrm{CO{-}CO}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CHMe}$.

Benzyloxaluric acid crystallises from alcoholic hydrochloric acid in needles, m. p. 157—159° (decomp.), and gives the oxaluric acid reaction with ammonia and calcium chloride; it was obtained only in small amount, has not been analysed, and might be possibly benzoyloxaluric acid.

5:5-*Dibromohydroxy*-1-*benzyl*-4-*methyluracil*, prepared by the action of bromine on 1-benzyl-4-methyluracil, is obtained as a white powder, decomposes at 98—105°, evolves benzaldehyde at 110°, and when boiled with absolute alcohol yields 5-*bromo*-1-*benzyl*-4-*methyluracil*, which crystallises in small needles, and decomposes at 238°. G. Y.

Pyrimidines: Synthesis of Uracil-5-carboxylic Acid. HENRY L. WHEELER, TREAT B. JOHNSON, and CARL O. JOHNS (*Amer. Chem. J.*, 1907, 37, 392—405).—Biscaro and Belloni (Abstr., 1905, i, 672) have isolated a substance from milk which they have termed "orotic acid" and which they regard as having the annexed structure. It is pointed out that the properties of this compound and the fact that it yields carbamide on oxidation, rendered it probable that it might be a pyrimidine and possibly either uracil-4-carboxylic acid,  $\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot CH}\end{matrix}>\mathrm{C\cdot CO_2H}$, or uracil-5-carboxylic acid,  $\mathrm{NH}<\begin{matrix}\mathrm{CO{-}{-}{-}NH}\\ \mathrm{CO\cdot C(CO_2H)}\end{matrix}>\mathrm{CH}$. Both these compounds have now been prepared; the latter is described in the present paper and an account of the former will be given later. Uracil-5-carboxylic acid is not identical with orotic acid, although it resembles it in many respects.


$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CH_2\cdot CO}\\ \mathrm{NH\cdot CO{-}CO}\end{matrix}$ or $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO\cdot CH_2}\\ \mathrm{NH\cdot CO\cdot CO}\end{matrix}$

When an alkaline, aqueous solution of ethyl-ψ-thiocarbamide hydrobromide is treated with ethyl ethoxymethylenemalonate, *ethyl* 2-*ethylthiol*-6-*oxypyrimidine*-5-*carboxylate*,  $\mathrm{NH}<\begin{matrix}\mathrm{C(SEt){=}{=}N}\\ \mathrm{CO\cdot C(CO_2Et)}\end{matrix}>\mathrm{CH}$, m. p. 131°, is obtained, which forms long, colourless prisms or needles, is soluble in hot alcohol, and has both acid and basic properties.

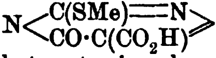
Ethyl uramidomethylenemalonate, $\mathrm{NH_2\cdot CO\cdot NH\cdot CH{:}C(CO_2Et)_2}$, m. p. 206° (decomp.), which is also produced in this reaction, crystallises in colourless prisms and has acid properties. 2-*Ethylthiol*-6-*oxypyrimidine*-5-*carboxylic acid*, m. p. 167°, forms colourless plates, dissolves readily in hot alcohol, and when warmed with hydrochloric acid yields mercaptan and uracil-5-carboxylic acid.

Uracil-5-*carboxylic acid*, m. p. 278° (decomp.), forms minute, colourless pyramids containing $1H_2O$, and is sparingly soluble in water. When this substance is heated alone above its m. p., uracil is produced. Uracil is also formed when the acid is heated with sulphuric acid in a sealed tube at 160—169° or boiled with concentrated hydrochloric acid. The *ethyl* ester, m. p. 236—237°; the *methyl* ester, m. p.

225—233° (decomp.), and the *ammonium*, *potassium*, *barium*, and *silver* salts are described. The *dimethyl* derivative, m. p. 254—256°, obtained by the action of methyl iodide on the di-silver salt, crystallises in small prisms; the corresponding *diethyl* derivative, m. p. 162—163°, forms clusters of blunt prisms.

When ethyl ethoxymethylenemalonate is treated with methyl-ψ-thiocarbamide hydriodide, ethyl 2-methylthiol-6-oxypyrimidine-5-carboxylate does not separate, but a basic *hydriodide*,

$$2C_8H_{10}O_3N_2S,HI,$$

is produced, which crystallises in needles. When this salt is warmed with potassium hydroxide, 2-*methylthiol*-6-*oxypyrimidine*-5-*carboxylic acid*,  $N{<}\begin{matrix}C(SMe){=}N\\CO\cdot C(CO_2H)\end{matrix}{>}CH$, m. p. 235°, is obtained, which separates from hot water in colourless prisms. E. G.

Condensations with Carbamide; Carbamide as a Source of Ammonia. OTTO KYM (*J. pr. Chem.*, 1907, [ii], 75, 323—327).—2-Hydroxy- and 2-mercapto-benziminazoles are prepared best by heating *o*-phenylenediamine with carbamide at 130—140° and with thiocarbamide at 170—180° respectively.

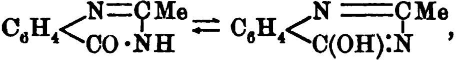
When heated with carbamide at 200—210° for eight hours, 2 : 4-dinitrophenol is converted to the extent of 75% into 2 : 4-dinitroaniline; dinitro-α-naphthol to the extent of 77% into dinitro-α-naphthylamine, and 3 : 5-dinitro-*o*-cresol to the extent of 47% into 3 : 5-dinitro-*o*-toluidine. G. Y.

Quinazolines. XVIII. 2 : 3-Dialkyl-4-quinazolones [4-Keto-2 : 3-dialkyldihydroquinazolines] and the Products obtained by Alkylating 2-Alkyl-4-quinazolones (4-Hydroxy-2-alkylquinazolines). MARSTON T. BOGERT and HARVEY A. SEIL (*J. Amer. Chem. Soc.*, 1907, 29, 517—536).—The existence of two series of derivatives in the quinazoline group, namely, oxygen derivatives, ·C(OR):N·, and nitrogen derivatives, ·CO·NR·, has long been recognised and the present work was undertaken with the object of ascertaining the relative extent to which these derivatives are produced in the alkylation of 4-hydroxyquinazolines (4-quinazolones) and the factors which determine their formation. A *résumé* is given of the results already obtained in this direction by various workers with α-hydroxypyridines (α-pyridones), carbostyrils (α-quinolones), *iso*carbostyrils (α-*iso*quinolones), 6-hydroxypyrimidines (6-pyrimidones), and 4-hydroxyquinazolines (4-quinazolones), and the following general conclusions are drawn. When alkylation is effected by methyl iodide or methyl sulphate in presence of alcohol and alkali hydroxide, the *N*-methyl derivative is always produced and, in some cases, small quantities of the *O*-ether also are formed. When an ethyl halide is used, the likelihood of obtaining the *O*-ether is considerably greater. On treating the silver salt with methyl iodide, both *O*- and *N*-derivatives are produced, but with ethyl iodide it frequently happens that the pure *O*-ether is obtained. Oxygen ethers are best prepared by the action of the alkyloxide on the chloro-derivatives. The *O*-ethers have higher m. p.'s and b. p.'s, are more likely to have an odour, are more readily hydrolysed by mineral acids, and are more stable towards oxidising agents than the corresponding *N*-derivatives. Many *O*-ethers have been converted into the corresponding *N*-isomerides by the action of heat or by other means, but the reverse transformation does not appear to have ever been effected.

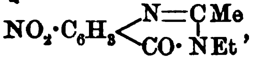
The preparation of the alkyldihydroquinazolines which are described was effected by the condensation of acylanthranils with ammonia and primary amines. 6-*Nitro-2-propionylaminobenzoic acid*,

$$NO_2\cdot C_6H_3(NH\cdot COEt)\cdot CO_2H,$$

m. p. 218° (corr.), forms hard, transparent crystals and is converted by acetic anhydride into the corresponding *anthranil*. 4-Keto-2 : 3-dimethyldihydroquinazoline (4-hydroxy-2 : 3-dimethylquinazoline),

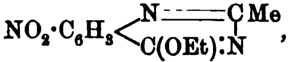


$C_6H_4<\begin{array}{l}N{=}CMe\\ CO\cdot NH\end{array} \rightleftharpoons C_6H_4<\begin{array}{l}N{=}CMe\\ C(OH){:}N\end{array}$, from acetylanthranil and methylamine, is identical with the compound obtained by Weddige (Abstr., 1887, 1044) by the methylation of 4-hydroxy-2-methylquinazoline. 7-*Nitro-4-keto-2-methyl-3-ethyldihydroquinazoline*,



$NO_2\cdot C_6H_3<\begin{array}{l}N{=}CMe\\ CO\cdot NEt\end{array}$, has m. p. 175° (corr.), and the corresponding 2-*methyl*-3-iso*amyl* compound has m. p. 117—118°. *Bromo*-5-*nitro*-3-*diacetylamino-4-keto-2-methyldihydroquinazoline* has m. p. 170°. 5-*Nitro-4-keto-2-ethyldihydroquinazoline* (5-*nitro-4-hydroxy-2-ethylquinazoline*) has m. p. 240° (corr.), and crystallises well from dilute alcohol. 5-*Nitro-4-keto-3-methyl-2-ethyldihydroquinazoline* and the corresponding 2 : 3-*diethyl* compound have m. p. 197—198° (corr.) and 181° (corr.) respectively.

On methylating 5-nitro-4-keto-2-methyldihydroquinazoline (Bogert and Chambers, Abstr., 1905, i, 615), 5-nitro-4-keto-2-ethyldihydroquinazoline, and 7-nitro-4-keto-2-methyldihydroquinazoline (Bogert and Steiner, Abstr., 1905, i, 946), the *N*-derivative only was obtained in each case, whether the reaction was carried out at the ordinary pressure or in a sealed tube. On ethylation, however, only the *O*-ethers were usually produced. 5-*Nitro-4-ethoxy-2-methylquinazoline*,



$$NO_2\cdot C_6H_3<\begin{array}{l}N{=}CMe\\ C(OEt){:}N\end{array},$$

m. p. 161° (corr.), can be repeatedly crystallised from alcohol without being converted into its *N*-isomeride. When the ethylation of 5-nitro-4-keto-2-ethyldihydroquinazoline takes place under the ordinary pressure, the pure *O*-ether is obtained, but if the reaction is carried out in a sealed tube a mixture of the *O*- and *N*-isomerides is produced. 5-*Nitro-4-ethoxy-2-ethylquinazoline*, m. p. 148—149°, is completely transformed into the corresponding *N*-derivative by recrystallisation from alcohol. 7-*Nitro-4-ethoxy-2-methylquinazoline*, m. p. 105—106° (corr.), is not changed on recrystallisation. 7-*Nitro*-4-iso*amyloxy-2-methylquinazoline*, m. p. 104° (corr.), forms large, flat plates, and does not show any tendency to undergo rearrangement. E. G.

New Dyes obtained from Triphenylmethane. MAURICE PRUD'HOMME (*Bull. Soc. ind. Mulhouse*, 1907, 79—81).—If reduced with zinc dust and hydrochloric acid in cooled aqueous or aqueous-alcoholic solution, *o*-nitrophenyl- and *m*-nitrophenyl-tetramethyldiaminodiphenylmethanes yield the corresponding *hydroxylamino-derivatives*, $CH(C_6H_4 \cdot NMe_2)_2 \cdot C_6H_4 \cdot NH \cdot OH$, which when heated with hydrochloric acid undergo transformation into 2-*amino*-5-*hydroxyphenyl*- and 5-*amino*-2-*hydroxyphenyl-tetramethyldiaminodiphenylmethane*, $CH(C_6H_4 \cdot NMe_2)_2 \cdot C_6H_3(NH_2) \cdot OH$, yielding a bluish-green and a greenish-yellow *dye* respectively on oxidation with lead dioxide and acetic acid. It is considered that the amino-groups are protected from the action of the oxidising agent by the *p*-hydroxyl groups. No advantage is gained by sulphonation of these aminohydroxy-dyes, as is the case in the formation of patent-blue.

The 2-amino-5-hydroxy-compound dissolves partially in ammonia, forming a blue solution, which is decolorised only slowly; the dye obtained on acidification of this solution has a purer shade than the crude dye. On diazotisation in presence of the theoretical amount of hydrochloric acid cooled by ice, the 2-amino-5-hydroxy-dye yields a blue solution, and when boiled is converted into 2 : 5-*dihydroxyphenyltetramethyldiaminodiphenylmethane*, $CH(C_6H_4 \cdot NMe_2)_2 \cdot C_6H_3(OH)_2$. The *product*, obtained on oxidation of this with lead dioxide and acetic acid, dyes unmordanted wool, or silk, black or grey, and cotton, mordanted with tannin and tartar emetic, grey. The same dihydroxy-compound must be obtained from the 5-amino-2-hydroxy-dye.

G. Y.

Some Semicarbazide Derivatives of *iso*Propionic Acid, Benzoic Acid, and Benzenesulphonic Acid.

Salomon F. Acree (*Amer. Chem. J.*, 1907, **37**, 361—369).—In connexion with the physico-chemical study of semicarbazides and urazoles, it became necessary to obtain substances of greater solubility in water than that possessed by most of the phenyl derivatives of these compounds. Some such substances, containing an acid side-chain, have already been prepared by Bailey and Acree (Abstr., 1900, i, 528), and others are now described.

Sodium p-*hydrazinobenzenesulphonate*,

$$NH_2 \cdot NH \cdot C_6H_4 \cdot SO_3Na, 2H_2O,$$

is white. By the action of potassium cyanate on *p*-hydrazinobenzenesulphonic acid, *a-semicarbazino*-p-*benzenesulphonic acid*, $NH_2 \cdot CO \cdot NH \cdot NH \cdot C_6H_4 \cdot SO_3H$, m. p. 243°, is obtained, which is very soluble in water; the *potassium* salt is white, crystalline, and anhydrous, and rapidly reduces potassium permanganate.

*a-Carbethoxysemicarbazino-a-*iso*propionitrile*,

$$NH_2 \cdot CO \cdot NH \cdot N(CO_2Et) \cdot CHMe \cdot CN,$$

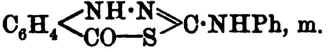
m. p. 173°, prepared by boiling *a*-semicarbazino*iso*propionitrile (Bailey and Acree, *loc. cit.*) with ethyl chlorocarbonate, crystallises from alcohol, is very soluble in acetone and fairly so in water or alcohol, and on hydrolysis yields *urazole-a-*iso*propionic acid.*

The *hydrobromide* of *o*-hydrazinobenzoic acid (Fischer, Abstr., 1880, 647), m. p. 207—210°, crystallises in needles.

*a-*o-*Semicarbazinobenzoic acid*, $NH_2 \cdot CO \cdot NH \cdot NH \cdot C_6H_4 \cdot CO_2H$, m. p. 225°, obtained by the action of potassium cyanate on *o*-hydrazinobenzoic acid, is very soluble in alcohol and fairly so in water, and yields a white *silver* salt which rapidly darkens. Potassium permanganate solution is instantly decolorised by the acid, and on adding sulphuric acid a red precipitate is formed which is probably the azocarbamide, $NH_2\cdot CO\cdot N_2\cdot C_6H_4\cdot CO_2H$.

When *potassium δ-phenyl-a-o-thiosemicarbazinobenzoate*,

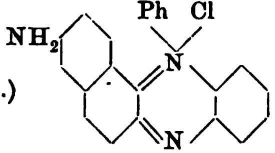
$$CO_2K\cdot C_6H_4\cdot NH\cdot NH\cdot CS\cdot NHPh,$$

obtained by the interaction of potassium *o*-hydrazinobenzoate and phenylthiocarbimide, is treated with dilute sulphuric acid, the corresponding *anhydride*,  $C_6H_4\left<\begin{matrix}NH\cdot N\\ CO—S\end{matrix}\right>C\cdot NHPh$, m. p. 238°, is produced, which is insoluble in alkali hydroxides. E. G.

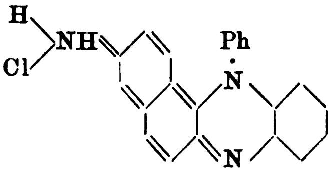
A New Type of Quinonoid Grouping in Onium Compounds.

Friedrich Kehrmann [and in part **C. Sabo** and **Werner-Gresly**] (*Ber.*, 1907, **40**, 1960—1966. Compare Willstätter and Parnas, this vol., i, 425).—The azonium dye of the constitution (I) differs in its physical and chemical properties from those of its isomerides which do not contain the amino-group in the *p*-position to any of the azine nitrogen atoms. The author represents a *bicyclo-p*-quinonoid group by (II):

(I.)



(II.)



which is an alternative formula for the azonium one.

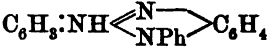
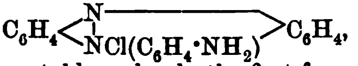
6-*Hydroxy*-1 : 2-*naphthaquinone* is prepared as follows. 2 : 6-Dihydroxynaphthalene is dissolved in an ice-cold aqueous solution of sodium hydroxide and converted into the corresponding azo-dye by coupling with diazobenzene chloride. When the dye is reduced by stannous chloride, 1-amino-2 : 6-dihydroxynaphthalene hydrochloride is formed, which, when oxidised by ferric chloride, is converted into the above quinone, which separates from acetone in brick-red leaflets, decomposing at about 165°. The solution of the quinone in cold water is golden-yellow. When added to a solution of *o*-aminodiphenylamine hydrochloride in alcohol, containing a little sulphuric acid, the quinone is readily dissolved, and from the solution, 7-*hydroxyphenyl*iso*naphthaphenazonium chloride* was obtained in glistening, reddish-brown needles. The *platinichloride*,

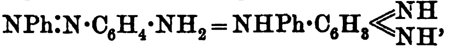
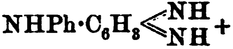
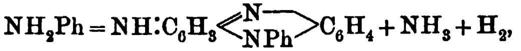
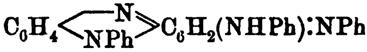
$$(C_{22}H_{15}ON_2Cl)_2,PtCl_4,$$

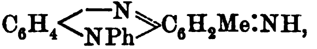
was analysed.

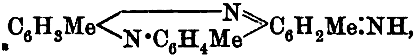
The condensation of 6-acetylamino-*β*-naphthaquinone with *o*-aminophenol is also described in this preliminary communication. A. McK.

*apo*Safranine and its Homologues.

Philippe Barbier and **Paul Sisley** (*Bull. Soc chim.*, 1907, [iv], 1, 468—474. Compare Abstr., 1906, i, 51, 989; 1907, i, 160).—Since commercial phenosafranine has been shown to consist of about 85% of the *as*-compound with 15% of the *s*-isomeride (*loc. cit.*), the *apo*safranine prepared from it by diazotisation and subsequent boiling of the diazo-compound with alcohol may have the constitution  $C_6H_3{:}NH\Big<{}^{N}_{NPh}\Big>C_6H_4$ or  $C_6H_4\Big<{}^{N}_{NCl(C_6H_4\cdot NH_2)}\Big>C_6H_4$, although possibly the latter may be unstable and only the first form will be produced in the reaction.

*apo*Safranine may be prepared by heating *p*-aminoazobenzene hydrochloride with aniline hydrochloride dissolved in water saturated with aniline in a closed vessel at 160—170°. The *hydrochloride* forms small copper-coloured crystals, and the *platinichloride* is a crystalline powder. The dye gives a magenta-red solution in water; the alcoholic solution is strongly dichroic, and that with sulphuric acid is violet, but becomes red on dilution. The dye can be diazotised and then coupled with naphtholsulphonic acids, yielding colouring matters which may have commercial applications. In addition to *apo*safranine there is formed a small quantity of Caro's "soluble induline." The formation of *apo*safranine is regarded as taking place according to the following equations: (1)  $NPh{:}N\cdot C_6H_4\cdot NH_2 = NHPh\cdot C_6H_3<{}^{NH}_{NH}$, (2)  $NHPh\cdot C_6H_3<{}^{NH}_{NH}$ +  $NH_2Ph = NH{:}C_6H_3\Big<{}^{N}_{NPh}\Big>C_6H_4 + NH_3 + H_2$, whilst Caro's "soluble induline," which is represented as  $C_6H_4\Big<{}^{N}_{NPh}\Big>C_6H_2(NHPh){:}NPh$, is regarded as being produced by a condensation, similar to that which takes place in the case of *apo*safranine, from some dianilinoquinoneanilimide, $NPh{:}C_6H_2(NHPh)_2{:}NH$, initially formed.

*Homo*apo*safranine*,  $C_6H_4\Big<{}^{N}_{NPh}\Big>C_6H_2Me{:}NH$, obtained by the action of diazoaminobenzene on *o*-toluidine hydrochloride, furnishes a *hydrochloride* which occurs as a microcrystalline, bronze powder; the aqueous solution is reddish-violet and the alcoholic solution is intensely dichroic. iso*Homo*apo*safranine*, obtained by the action of *o*-toluidine hydrochloride on *p*-aminoazobenzene, closely resembles its isomeride.

*Tolu*apo*safranine*,  $C_6H_3Me\Big<{}^{N}_{N\cdot C_6H_4Me}\Big>C_6H_2Me{:}NH$, obtained by the action of *o*-toluidine hydrochloride on *p*-aminoazotoluene, furnishes a reddish-brown *hydrochloride*, which is very soluble in water.

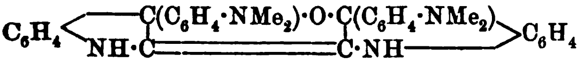
All these *apo*safranines dye cotton and silk, previously treated with tannic acid, in red shades, which become more violet as the molecular weight increases, but they are inferior in tinctorial power when compared with the corresponding safranines. T. A. H.

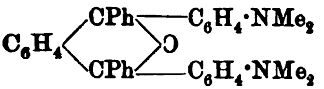
So-called "Dihydrotetrazine." MAX BUSCH (*Ber.*, 1907, 40, 2093—2095).—In addition to the evidence cited by Curtius, Darapsky, and Müller (this vol., i, 262, 451), the author (Abstr., 1901, i, 616) showed formerly that the so-called urazines are in reality aminotriazoles. Thus from ethyl phenylmethylphenylcarbazidecarboxylate a triazole, anilinophenylmethylurazole, was obtained, which on elimination of methyl formed diphenylurazine.

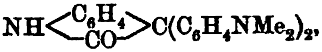
The paper further contains a polemical discussion of the views of

Bülow and Stollé as to the interpretation of urazines as tetrazines or triazoles. E. F. A.

Extension of the Friedel-Craft Reaction. Albin Haller and Alfred Guyot (*Compt. rend.*, 1907, **144**, 947—951).—*tert.*-Aromatic amines and certain *sec.*-amines, for example, diphenylamine, alone or dissolved in a neutral solvent, condense readily in presence of aluminium chloride with a great number of organic compounds, notably the oxalic esters and the ketones. In the latter case, the amine appears to be simply attached to the carbon of the carbonyl group, giving rise to a *tert.*-carbinol group, thus: $C(OH)\cdot C_6H_4\cdot NR_2$, with in some cases the subsequent elimination of one or more mols. of water. In this respect the reaction somewhat resembles the condensations brought about by the action of zinc chloride. The reaction does not take place unless the ketone is distinctly acidic in character; thus, whilst benzophenone condenses readily with dimethylaniline in presence of aluminium chloride, no reaction takes place between Michler's tetramethyldiaminobenzophenone and the amine.


$C_6H_4<\begin{matrix}C(C_6H_4\cdot NMe_2)\cdot O\cdot C(C_6H_4\cdot NMe_2)\\ NH\cdot C=C\cdot NH\end{matrix}>C_6H_4$



Indigotin condenses with dimethylaniline to form a *product*, m. p. 272°, which crystallises in orange leaflets, and probably has the annexed constitution. With benzil the same amine furnishes a *substance*, $C_{30}H_{30}ON_2$, m. p. 214°, which crystallises in pale yellow needles, and may have the formula $O<\begin{matrix}CPh\cdot C_6H_4\cdot NMe_2\\ CPh\cdot C_6H_4\cdot NMe_2\end{matrix}$, or $CPh(C_6H_4\cdot NMe_2)_2\cdot COPh$, or $CPh_2(C_6H_4\cdot NMe_2)$ (?). It does not yield a semicarbazone. With *o*-dibenzoylbenzene two isomeric, colourless, crystalline *substances*, $C_{36}H_{34}ON_2$, are produced; the one has m. p. 186°, and the other, m. p. 226°. These may be the two possible stereoisomerides of which the *cis*-form would have the annexed formula, or, as the result of transformation of dihydrobenzo*iso*furan derivatives first formed (compare Guyot and Catel, Abstr., 1906, i, 761), they may be anthracene compounds of the following constitution, $C_6H_4<\begin{matrix}CPh\cdot(C_6H_4\cdot NMe_2)\\ CPh(OH)\end{matrix}>C_6H_3\cdot NMe_2$ or $NMe_2\cdot C_6H_4\cdot C(OH)<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>CPh\cdot C_6H_4\cdot NMe_2$. Ethyl phenylglyoxalate condenses with dimethylaniline to form *ethyl tetramethyldiaminotriphenylacetate*, $CPh(C_6H_4\cdot NMe_2)_2\cdot CO_2Et$, m. p. 98°, which crystallises in colourless leaflets, and when warmed with sulphuric acid evolves carbon dioxide and is transformed into malachite-green. With benzophenone, *p*-dimethylaminotriphenylcarbinol (Ehrlich and Sachs, Abstr., 1904, i, 196) is supposed to be produced, but the product obtained was a brown, viscous mass instead of the crystalline material described under this name by Baeyer and Villiger (Abstr., 1904, i, 786). It yielded when kept, but more readily on treatment with zinc and acetic acid, crystals of O. Fischer's dimethylaminotriphenylmethane and dissolved in acids with the production of a fine red colour. Isatin condenses with dimethylaniline under the conditions described to produce the compound,  $NH\left<\begin{smallmatrix}C_6H_4\\CO\end{smallmatrix}\right>C(C_6H_4NMe_2)_2$, already described by Baeyer and Lazarus (Abstr., 1886, i, 154). Similar products are obtained by the condensation of anthraquinone, β-methylanthraquinone, and β-dimethylaminoanthraquinone with dimethyl- or diethyl-aniline. T. A. H.

Azophenols. II. Richard Willstätter and Max Benz (*Ber.*, 1907, 40, 1578—1584. Compare Abstr., 1906, i, 990).—In a previous communication, the authors showed that *p*-azophenol exists in two forms, which are probably geometrical isomerides. Additional evidence in favour of this view is now submitted; the isomerism persists with the acetyl derivatives.

α-Azophenol exists in two modifications; the form, which is dehydrated by heat, is designated as α_1, and the form, which is dehydrated at the ordinary temperature under diminished pressure, as α_2. The α_1-form does not absorb water from moist air, but quickly absorbs ammonia; the α_2-form, on the other hand, absorbs $1H_2O$, is not so quickly acted on by ammonia as its isomeride, and, when heated, is transformed into the α_1-form.

β-Azophenol also exists in two varieties which closely resemble one another. The reduction product of quinoneazine is designated as the β_1-variety, whilst the β_2-variety is obtained from a moist ethereal or concentrated sulphuric acid solution of the β_1-variety; β_1 is stable, whilst β_2 is readily transformed into the α-form.

The anhydrous α-form is dark green, whilst the anhydrous β-form is red.

α-Azophenol remains unchanged in alkaline solution, and may be precipitated from it unchanged by the addition of acid. If, however, some of the β_1-form is added to the alkaline solution of the α-form, the latter is transformed into the stable β_1-form.

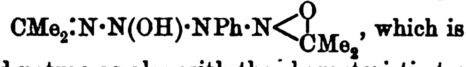
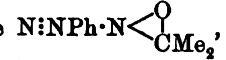
The α- and β-forms are convertible one into the other by means of sulphuric acid.

p-*Azophenyl acetate*, $OAc\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot OAc$, obtained by the acetylation of *p*-azophenol by Thiele's method or by acetylating *p*-azophenol in alkaline solution, separates from glacial acetic acid in yellow prisms and needles, m. p. 198—199°. The specimen of *p*-azophenyl acetate, obtained in the manner indicated, is the *α-form* irrespective of whether α- or β-azophenol is used. The pure β-p-*azophenyl acetate* is present in the freshly-prepared alkaline solution of β_1-*p*-azophenol.

β-Azophenol may be converted into α-azophenol by acetylation, recrystallisation of the product from glacial acetic acid, and subsequent hydrolysis.

p-*Azophenyl benzoate*, $OBz\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot OBz$, separates from benzene or xylene in reddish-yellow leaflets and is characterised by having two sharp melting points, 210·5—211·5° and 249—251°; it forms liquid crystals.

p-Azoanisole, $OMe\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot OMe$, obtained by methylating either *a*- or β-azophenol by methyl sulphate, separates from methyl alcohol in prisms or leaflets, m. p. 160·5—162·5° (Rotarski gives m. p. 160—162°). A. McK.

Diazo-oximes. H. W. Bresler, W. H. Friedemann, and Julius Mai (*Annalen*, 1907, **353**, 228—241. Compare Abstr., 1892, 163, 1079; 1906, i, 321; Bamberger, Abstr., 1899, i, 589).—This is an investigation of the constitution of the diazobisoximes, which is discussed in the light of the experimental results described below. It is concluded that benzenediazobisacetoxime is represented best by the formula  $CMe_2{:}N\cdot N(OH)\cdot NPh\cdot N{<}\overset{O}{\underset{CMe_2}{|}}$, which is shown to agree with the acid nature as also with the characteristic transformations of the diazobisoximes. The formation of such a substance is pictured as taking place in two stages, the hypothetical intermediate product having the structure  $N{:}NPh\cdot N{<}\overset{O}{\underset{CMe_2}{|}}$, and the second stage being the addition of acetoxime to the tervalent diazonium nitrogen atom (compare Hantzsch, Abstr., 1900, i, 703).

From an examination of the products obtained when *p*-tolyldiazobisacetoxime is heated carefully, it is concluded that one of the acetoxime groups in the diazobisacetoxime must be readily split off, leaving the unstable complex, $C_{10}H_{13}ON_3$, which decomposes partially into *p*-diazotolueneimide and acetone, and for the remainder reacts with a small amount of water, assumed to be present, forming *p*-toluidine, acetone, and nitrous oxide. This view of the reaction, however, does not explain the formation of a considerable volume of nitrogen. When heated with alcohol at 50—60°, *p*-tolyldiazobisacetoxime yields *p*-toluidine and *p* diazotolueneimide. Since *p*-toluidine is the main product in both decompositions, it appeared probable that the grouping $C_6H_4Me\cdot NH\cdot$ is present in the diazobisacetoxime molecule which might be formed by the action of acetoxime on the nitrosoamine form of the diazohydrate: $C_7H_7\cdot NH\cdot NO + 2CMe_2{:}N\cdot OH = H_2O + C_7H_7\cdot NH\cdot N(O\cdot N{:}CMe_2)_2$. This assumption, however, is not supported by the behaviour of nitrosoamines with oximes; sodium phenylnitrosoamine does not react with acetoxime, whilst sodium *p*-nitrophenylnitrosoamine reacts only slowly, and apparently after isomeric change of the nitrosoamine into the diazo-hydrate, since the free nitrosoamine, which readily undergoes the transformation, reacts with acetoxime in dilute alcoholic solution almost instantaneously.

When reduced with sodium amalgam in cooled alcoholic solution, *p*-tolyldiazobisacetoxime forms *p*-toluidine, *iso*propylamine, and hydroxylamine; the *p*-toluidine is obtained in an almost quantitative yield.

The action of dilute hydrochloric acid on the diazobisoximes leads to the formation of the aldehyde or ketone, the oxime, and the diazoimide; this reaction has been studied in the case of benzenediazobis-4-dimethylaminobenzaldoxime, which is found to yield diazobenzeneimide, *p*-dimethylaminobenzaldoxime, and *p*-dimethylaminobenzaldehyde in amounts closely approximating to molecular proportions. Similarly, acetoxime, *p*-diazotolueneimide, and acetone are obtained in molecular proportions by the action of hydrogen chloride on *p*-toluenediazobisacetoxime in ethereal solution.

The acid character of the diazobisoximes, observed first by Bamberger (*loc. cit.*), is confirmed by the formation of a *copper* salt, $C_{24}H_{32}O_8N_{10}Cu$. The red solutions, formed in the coupling of diazohydrates with oximes, which become colourless on dilution, must contain unstable alkali salts of the diazobisoximes; it is found now that *p*-nitrobenzenediazobisacetaldoxime forms, in alkaline solution, a stable red salt, the solution remaining red on addition of an excess of ammonium chloride, and yielding yellow to brown precipitates with metallic salts. G. Y.

[**4 : 4′-Diaminodi-*p*-phenoxybenzene and its Azo-derivatives.**] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 178803).—4 : 4′-*Diaminodi*-p-*phenoxybenzene*, $C_6H_4(O\cdot C_6H_4\cdot NH_2)_2$, m. p. 170°, was obtained by condensing *p*-chloronitrobenzene with the dry potassium derivative of quinol and then reducing the resulting dinitro-compound; it crystallises from alcohol in colourless needles. Its hydrochloride separates in long, colourless, soluble needles, and is precipitated by strong hydrochloric acid. The bisdiazo-chloride readily combines with 6-amino-*α*-naphthol-3-sulphonic acid and other naphtholsulphonic acids to furnish substantive dyes, which have a brilliant red shade and are fast to acids. A series of these azo-derivatives is tabulated in the patent. G. T. M.

Formation of Hydrols and Aldehydes. Action of Diazohydroxides on Amino-derivatives of Di- and Tri-phenylmethane. ÉMILE SUAIS (*Bull. Soc. ind. Mulhouse*, 1907, 75—78).—Diazo-hydroxides react with dialkylamino-derivatives of di- and triphenylmethane, forming hydrols or aldehydes and dialkylaminobenzeneazo-compounds; in the case of tetramethyldiaminotriphenylmethane the reaction takes place according to the scheme: I, $CHPh(C_6H_4\cdot NMe_2)_2 + N_2R\cdot OH = OH\cdot CHPh\cdot C_6H_4\cdot NMe_2 + N_2R\cdot C_6H_4\cdot NMe_2$, or, II, $CHPh(C_6H_4\cdot NMe_2)_2 + 2N_2R\cdot OH = C_6H_5\cdot CHO + H_2O + 2N_2R\cdot C_6H_4\cdot NMe_2$. The reaction, which takes place in neutral, alcoholic-aqueous solution at the ordinary temperature, has been carried out with the diazo-hydroxides derived from *p*-sulphanilic acid, Dahl's No. III acid, and *m*-nitroaniline, on the one hand, and, on the other, with leucomalachite-green, leucohexamethyl-violet, tetramethyldiaminodiphenyl-*α*-ethylaminonaphthylmethane, tetramethyldiaminodiphenylmethane, and tetramethyldiaminobenzhydrol.

The following quantitative results were obtained with the diazoderivative of Dahl's No. III acid; the percentages quoted are those calculated from the above schemes I and II. Leucohexamethylviolet with 1 mol. of the diazo-hydroxide yields 55—60% of tetramethyldiaminobenzhydrol. Tetramethyldiaminodiphenyl-*α*-ethylaminonaphthylmethane with 1 mol. of the diazohydroxide yields 70% of tetramethyldiaminobenzhydrol. Leucomalachite-green yields with 1 mol. of the diazo-hydroxide 70%, or with 2 mols. 60%, or with excess (3 mols.) 80%, of the amount required by II, of the azo-compound. Tetramethyldiaminobenzhydrol yields 85% of the azo-compound, the total yield remaining unchanged on addition of a second mol. of the diazo-hydroxide; hence the *p*-dimethylaminobenzaldehyde formed by the first stage does not react with the diazo-hydroxide. Tetramethyldiaminodiphenylmethane yields 80% of the azo-compound with 1 mol., or 70% with 2 mols., of the diazo-hydroxide; as in the first case half of the diphenylmethane base is recovered unchanged, the diazo-hydroxide must attack the two groups, $\cdot C_6H_4\cdot NMe_2$, simultaneously, or the possible intermediate product, dimethylaminobenzyl alcohol reacts with the diazo-hydroxide more readily than does the diphenylmethane base.

The reaction described offers a practical method of preparing hydrols and aldehydes. G. Y.

Chemistry of Globulin. WILLIAM SUTHERLAND (*Proc. Roy. Soc.*, 1907, *B*, 79, 130—154).—The experimental results obtained by Hardy (Abstr., 1906, i, 121) and Mellanby (*ibid*, 122) may be represented by simple formulæ which show that the solution of globulin and its precipitation take place under simple conditions of chemical equilibrium.

For the precipitation of globulin by excess of ammonium sulphate the equation $p(1+p)=28{\cdot}8(c-0{\cdot}152)$, where p is the fraction which the precipitated globulin is of the whole and c the concentration of the sulphate in grams per c.c., holds good. Formulæ are applied to the precipitation of globulin by acids from solution in neutral salts, and from these it appears that three compounds of globulin react in producing the precipitate.

A theory of the colloidal state is promulgated. According to this a colloid consists of molecules which are chemically united neighbour to neighbour by the action of valencies which are usually latent. Cases of multiple valency are best accounted for by the electron theory of valency due to Helmholtz, with the assumption that a single atom can contain both negative and positive electrons. According to the author's view the term molecule ceases to have a useful meaning as applied to a colloid and the term *semplar* is used to denote the structure which is repeated like a pattern in three dimensions through a colloid. By suppression of the colloid producing valencies a mass of semplars is converted into a collection of separate molecules. The theory is applied to the various phenomena met with in the study of colloids.

Hardy's experiments on conductivities of globulin solutions can be expressed by means of formulæ which admit of very simple interpretation. At infinite dilution, the hydrochloric acid compound of globulin is completely hydrolysed, the conductivity being that due to the ionised hydrochloric acid, the part due to the globulin being negligible. For other concentrations, the ratio of combined and free hydrochloric acid can be calculated. In the compounds with ammonium and sodium hydroxides, half of the base combines with the globulin in a way which proves it to be an acid, the resulting salt being completely dissociated; the remaining half of the base which is required to dissolve globulin combines with it by addition.

Globulin is shown to have a probable molecular mass 40,000 and basicity 2, or mass 60,000 and basicity 3. A group, $C_{12}H_{20}O_4N_3$, related to polypeptides and peptones is shown to be the predominant structure in albumins. The discrepant results of different experimenters on the precipitation of albumin by heavy metals fall into harmony when it is proved that they precipitated different integral numbers of a group such as this in combination with an equivalent of heavy metal. J. J. S.

Globulin Precipitated from Human Blood Serum by Acetic Acid. Georges Patein (*J. Pharm. Chim.*, 1907, [vi], **25**, 470—476).—The precipitate obtained by neutralising the diluted serum with acetic acid is insoluble in water and soluble in acetic acid or sodium carbonate solution and is composed of two globulins, the chief constituent being soluble in 0·6% or more concentrated solutions of sodium chloride and the other in 10% or stronger solutions of the same salt. The precipitate is coagulated in suspension in water or in solution in dilute acetic acid at 56° and in salt solution at 78°. These facts indicate that the material is not a nucleoproteid, a fibrino-globulin, or a casein, and it is further distinguished from the last of these by containing no phosphorus, although it contains some sulphur.

T. A. H.

Mono-amino-acids of Lactalbumin. Emil Abderhalden and Hugo Přibram (*Zeitsch. physiol. Chem.*, 1907, **51**, 409—414).—The lactalbumin was prepared from cow's milk. It was free from phosphorus, and therefore from caseinogen. Whether it was absolutely free from lacto-globulin is uncertain; parts of it at any rate yielded no glycine, and glycine is usually obtained from globulins. A further examination of lacto-globulin will, however, be necessary. The mono-amino-acids obtained in parts per cent. of the albumin were: alanine, 2·5; valine, 0·9; leucine, 19·4; proline, 4·0; aspartic acid, 1·0; glutamic acid, 10·1; phenylalanine, 2·4, and tyrosine, 0·85.

W. D. H.

Increase in Weight in the Hydrolysis of Casein. John H. Long (*J. Amer. Chem. Soc.*, 1907, **29**, 295—299).—In a previous paper (this vol., i, 367) it has been shown that when casein has been submitted to prolonged digestion with pepsin and dilute hydrochloric acid, the residue left on evaporating the liquid to dryness contains combined hydrogen chloride. A series of experiments has now been made with the casein of cow's milk in order to determine the rate of increase in weight due to the addition of hydrogen chloride, or water, or both. The mixtures of casein, pepsin, and dilute hydrochloric acid were maintained at 40°, and the weight of the residue was determined at intervals. The results are tabulated, and show that the increase is due to both water and hydrogen chloride. It is found that the products are relatively stable, and that on prolonged heating they lose more water than hydrogen chloride. A large proportion of the water and acid is added during the final evaporation, rather than during the prolonged digestion at 40°. The amount of water added in the actual digestion does not vary much after ten days or so, but the hydrogen chloride is added more slowly and shows a gradual increase. On the other hand, in the final evaporation, there is a marked increase in the amount of water added in the case of the products of the most prolonged digestions and a relatively small increase in the hydrogen chloride. It is found that 480 mg. of casein finally experience a total increase of 70 mg. of added water and 110 mg. of acid.

It is noteworthy that the sensitiveness of the product to phenolphthalein becomes less as the digestion progresses. The final colour reaction recalls that observed in titrations made in presence of traces of ammonium salts, and evidently indicates the accumulation of amino-compounds, which show an analogous behaviour.

It is suggested that *p*-nitrophenol will probably be found a useful indicator for the estimation of total mineral acids in digestion experiments. E. G.

The Salting-out of Caseinogen and Casein by Sodium Chloride. SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1907, 9, 311—321).—Two per cent. solutions of sodium caseinogenate and of sodium caseinate were prepared; no precipitation occurs on saturating such solutions with pure sodium chloride. Common salt, however, which contains about 0·4% of calcium and 0·05% of magnesium causes complete precipitation of the proteins in combination with the alkali earths. The calcium ions can be replaced by barium or magnesium, but the quantity of these necessary is about three times that of the calcium ions. W. D. H.

The Relation of Whey-protein to Rennet Action. SIGVAL SCHMIDT-NIELSEN (*Beitr. chem. Physiol. Path.*, 1907, 9, 322—332).—Pure solutions of caseinogen, prepared by acid precipitation or salting-out, when acted on by rennet, yield about 4% of their nitrogen in the form of whey-protein, which is regarded as a cleavage product of the caseinogen. The mucous membrane of the calf's stomach yields in addition to rennet a protease, which, acting on the casein, yields an increase in the yield of whey-protein. This protease follows the Schutz-Borissow law. W. D. H.

Behaviour of Caseinogen towards Ozone. CARL D. HARRIES and KURT LANGHELD (*Zeitsch. physiol. Chem.*, 1907, 51, 342—373).—Evidence was obtained that ozonisation of caseinogen leads to the production of comparatively large amounts of the cleavage products of protein. These were separated by lead acetate or by successive treatment with phosphotungstic acid and lead acetate. Little or no leucine was obtained. W. D. H.

Behaviour of Protein Cleavage Products and Certain Sugars with Ozone. CARL D. HARRIES and KURT LANGHELD (*Zeitsch. physiol. Chem.*, 1907, 51, 373—383).—The fatty amino-acids, including serine, are not altered by ozone. The same is true for amino-acetaldehyde, asparagine, and guanidine. The aromatic cleavage products of protein (phenylalanine, tyrosine, and tryptophan) are altered with the formation of reducing substances. This occurs best in an alkaline, and least in an acid solution. The chemistry of the change was not made out. The diamino-acids have not yet been examined.

The action of ozone on dextrose is very small; mannitol is changed into mannose and lævulose; dulcitol probably yields galactose.

W. D. H.

The Monoamino-acids of Crystallised Oxyhæmoglobin. Emil Abderhalden and Louis Baumann (*Zeitsch. physiol. Chem.*, 1907, 51, 397—403).—Globin was prepared from the crystallised oxyhæmoglobin of dog's blood; the amount of hæmatin in the oxyhæmoglobin is 4·2%. The following numbers give the percentages of monoamino-acids obtained from the globin as compared with those previously obtained from globin prepared from the horse:

	Dog.	Horse.
Glycine	Traces	—
Alanine	3·0	3·0
Valine	1·0	—
Leucine	17·5	20·9
Proline	4·5	1·5
Aspartic acid	2·5	3·4
Glutamic acid	1·2	1·1
Phenylalanine	5·0	3·5

W. D. H.

Hæmopyrrole. William Küster (*Ber.*, 1907, 40, 2017—2020. Compare Abstr., 1902, i, 845; 1904, i, 647).—The imide obtained by the oxidation of the acid hæmopyrrole is identical with synthetical methylethylmaleinimide. The slightly basic hæmopyrrole also yields an imide from which a small amount of methylethylmaleinimide has been isolated. Hæmopyrrole is thus a mixture of two pyrrole derivatives, the acid constituent is 3-methyl-4-ethylpyrrole, and the basic constituent is 3-methyl-4-ethylpyrroline or 2:4-dimethyl-3-ethylpyrrole or -pyrroline.

J. J. S.

A New Crystalline Derivative of Hæmin. William Küster and Karl Fuchs (*Ber.*, 1907, 40, 2021—2023).—When dehydrochloridehæmin is extracted for some time with ether in order to remove the last traces of aniline, a mixture of two crystalline products separates in the flask. These may be separated by means of boiling alcohol from which the one compound, $C_{36}H_{36}O_8N_4$, termed *ethyl anhydrohæmaterate*, separates as pointed, yellowish-red needles, m. p. 205—210°. The formation of this compound is probably due to the partial esterification of the hæmin to $C_{36}H_{36}O_4N_4ClFe$, and the withdrawal of the iron by hydrochloric acid yielding $C_{36}H_{38}O_4N_4$ from which the new compound is obtained by the elimination of water. It does not dissolve in alkalis, but is soluble in hydrochloric acid.

J. J. S.

Thymus-nucleic Acid. Walter Jones and C. R. Austrian (*J. Biol. Chem.*, 1907, 3, 1—10).—By the action of nuclease, thymus-

nucleic acid does not yield xanthine; the xanthine formed by more violent hydrolytic methods must therefore originate in guanine groups, or in guanine itself. Hydrolysis at high temperatures destroys a large amount of purine products, especially guanine. The quantities of guanine and hypoxanthine (equivalent to adenine) formed by ferment action are nearly proportional to the molecular weights of the bases. This is evidence that the two bases result from the same nucleic acid.
W. D. H.

The Rendering Insoluble of Gelatin by Benzoquinone. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEWEYETZ (*Bull Soc. chim.*, 1907, [iv], 1, 428—431. Compare Abstr., 1906, i, 614, 915, 999).—When a dilute solution of benzoquinone is added to one of gelatin, the latter "sets" in about the same time as when no benzoquinone is present, but the product no longer liquefies on warming. Gelatin can be rendered insoluble by the action of a solution containing 0·001% of benzoquinone, but with so dilute a solution the action proceeds slowly. The product is much more stable than that obtained by the action of formaldehyde on gelatin. Its colour varies from pink to reddish-brown, depending mainly on the colour and strength of the solution of benzoquinone used to produce it. It swells slightly under the action of cold water and remains insoluble in water even after prolonged ebullition. It is not dissociated into its constituents by acids, alkali carbonates or hydroxides or ammonia, but acids and alkalis produce eventually decomposition of the gelatin, this action being the more rapid the more concentrated is the solution of the reagent employed. Ammonia and the alkali carbonates, on the contrary, act very slowly in the cold even in very concentrated solution. T. A. H.

Monoamino-acids from Syntonin prepared from Ox-flesh. EMIL ABDERHALDEN and TAKAOKI SASAKI (*Zeitsch. physiol. Chem.*, 1907, 51, 404—408).—Isolation of the muscle-proteins was not attempted. The syntonin or acid-albumin prepared from ox-flesh, after separation of the humin which is formed yielded the following amino-acids in parts per cent.: glycine, 0·5; alanine, 4; valine, 0·9; leucine, 7·8; proline, 3·3; aspartic acid, 0 5; glutamic acid, 13·6; phenylalanine, 2·5; tyrosine, 2·2.
W. D. H.

Relation of Electrolytes to Lecithin and Kephalin. WALDEMAR KOCH (*J. Biol. Chem.*, 1907, 3, 53—56).—The precipitating action of calcium salts in solutions of lecithin is largely hindered by sodium chloride. According to A. P. Mathews' views, the dissolving action of the chlorine ion will explain this. The greater sensitiveness of kephalin to precipitation by cations can be explained by its more acid properties.
W. D. H.

Influence of Ions on Catalysis produced by Pepsin and Trypsin. WILLIAM N. BERG and WILLIAM J. GIES (*J. Biol. Chem.*, 1907, 2, 489—546).—Beyond the fact well known previously that hydrogen ions favour the action of pepsin, and hydroxyl ions that of trypsin, the present research led to negative results. Disparities in the velocity, quality, and extent of digestion by pepsin occur in solutions of different acids, whether they are present in equal masses, equal numbers of molecules, of hydrogen atoms, or of hydrogen ions. The action of trypsin is equally irregular. W. D. H.

Fermentative Decomposition of Dipeptides. HANS EULER (*Zeitsch. physiol. Chem.*, 1907, 51, 213—225. Compare Abderhalden and Teruuchi, Abstr., 1906, ii, 464, Abderhalden and Schittenhelm, this vol., i, 104).—The decomposition of glycylglycine by means of erepsin in the presence of sodium hydroxide has been studied as a time reaction by means of electrical conductivity determinations.

The velocity varies considerably with the concentration of the alkali, the maximum being reached when the concentration of the sodium hydroxide is from 0·04—0·06. A considerable proportion of the added alkali is not present as such, but is combined with the glycylglycine and also with the erepsin preparation; if these facts are taken into consideration the optimal concentration of the free alkali is 0·000012. The dissociation constants of glycylglycine, leucylglycine and alanylglycine have been determined as acids and also as bases.

The values are:

	K_A	K_B
Glycylglycine	$1{\cdot}8 \times 10^{-8}$	2×10^{-11}
Leucylglycine	$1{\cdot}5 \times 10^{-8}$	3×10^{-11}
Alanylglycine	$1{\cdot}8 \times 10^{-8}$	2×10^{-11}

The decomposition of glycylglycine is a reaction of the first order and the velocity constant has the same value until some 50% is decomposed. It then decreases, mainly owing to the decomposition of the erepsin and not to the retarding effects of the products of decomposition. The constant is almost independent of the concentration of the peptide, provided the concentration ratio ferment/substrate is within certain limits, but the constant is practically proportional to the concentration of the enzyme, and Schütz-Borissow's rule does not hold. When extremely small amounts of ferment are present, K increases more rapidly than the concentration of the ferment. J. J. S.

Opium Toxins. WOLFGANG WEICHARDT and HERMANN STADLINGER (*Biochem. Zeitsch.*, 1907, 3, 431—438)—Protein splitting "antigens" of a fatigue producing character are found not only in the animal, but also in the vegetable, kingdom. That which is present in opium can be obtained in a pure condition by dialysis after removal of the alkaloids, and the opinion is expressed that the complex physiological action of opium is in part due to its presence. W. D. H.

Oxidising Ferments. I. The Mode of Action of Tyrosinase. ROBERT CHODAT and STAUB (*Arch. Sci. phys. nat.*, 1907, [iv], 23, 265–277).—The oxidising action of tyrosinase has been studied. A solution of the ferment is most conveniently obtained from *Russula delica* or *Solanum tuberosum*. The red colour which the ferment gives with tyrosine is not obtained with the albumoses, but its production with glycyltyrosine anhydride indicates that other peptides may give the reaction.

Contrary to Bach's observations, it is found that hydrogen peroxide diminishes the activity of tyrosinase and frequently inhibits its action on tyrosine. Gonnermann's conclusion (*Pflüger's Archiv*, 1900, 82) that tyrosinase is not an oxidising, but a hydrolytic ferment is refuted by the results of experiments in an atmosphere of carbon dioxide; these show clearly that oxygen is necessary for the action, and that the action of the ferment is not simply the production by hydrolysis of an easily oxidisable product.

The rate of oxidation of tyrosine is very much smaller when leucine is added to the solution, but an explanation of this has not yet been obtained. The activity of the ferment increases with temperature up to 61°; at 66° it becomes inactive. At small concentrations the activity is proportional to the concentration of the ferment, but at higher concentrations the rate is expressed by the formula $kc+b$, where c is the concentration, and k and b constants. This influence of the concentration is similar to that already observed in the action of laccase (from *Lactarius vellereus*) on pyrogallol. H. M. D.

Oxidising Ferments. II. Distribution [Phenomena] in the Action of Peroxydase in Presence of Catalase. ROBERT CHODAT and J. PASMANIK (*Arch. Sci. phys. nat.*, 1907, **23**, 386—393. Compare preceding abstract).—The rate at which iodine is liberated from potassium iodide solution acidified with acetic acid by (1) hydrogen peroxide, (2) hydrogen peroxide + peroxydase, (3) hydrogen peroxide + catalase, and (4) hydrogen peroxide + catalase + peroxydase has been compared. In all the experiments the concentration of the peroxydase was 0·1%, but that of the catalase was varied from 0·00025 to 1·0%. The accelerating effect of the peroxydase is greatly diminished in presence of very small quantities of catalase, but even when the catalase is present in large excess the accelerating influence of the peroxydase on the liberation of iodine from the mixture of peroxide and iodide is clearly distinguishable. With increasing concentration, the retardation resulting from the catalase appears to approximate to a limiting value. Loew's view, that if hydrogen peroxide were formed in the metabolic processes taking place in the cell, it would be immediately destroyed by the catalase even in presence of oxidising ferments, is incompatible with these experimental results. The data rather indicate that distribution phenomena occur when peroxydase and catalase are both present in the system. H. M. D.

Oxidising Ferments. III. A Hypothesis as to the Action of Ferments. ROBERT CHODAT and J. PASMANIK (*Arch. Sci. phys. nat.*, 1907, **23**, 394—400. Compare preceding abstracts).—The action of ferments is supposed to be connected with the electrolytic dissociation of water, the degree of dissociation being increased in the presence of ferments which unite with the hydrogen and hydroxyl ions to form complex acid or basic groups capable of specific ferment action. In support of this view it was found that the electrical conductivity of 0·1% solutions of catalase, peroxydase, and pepsin was much smaller after boiling than before. Other known facts are recorded as evidence in support of the authors' hypothesis. H. M. D.

Zymoids. A. R. Bearn and Wilhelm Cramer (*Biochem. J.*, 1907, **2**, 174—185. Compare Abstr., 1906, i, 780).—Solutions of enzymes which have been heated at 56—60° for twenty to thirty minutes inhibit the activity of the unheated enzyme. The inhibition disappears by exposure to 100° as a rule. The inhibitory power varies in different preparations of the same enzyme. It is not due to an anti-ferment, but is brought about by a reaction between the substrate and substances present in the inactivated enzyme. These substances dialyse very slowly through parchment paper. In the case of pepsin they are not specific for each species. These facts point to the existence of zymoids which are probably preformed in the enzyme preparations. Zymoids, like enzymes, differ in their resistance towards heat, and different enzyme preparations vary in the amount of zymoids they contain. W. D. H.

Chemical Reaction Showing Green Luminescence. Edgar Wedekind (*Chem. Zentr.*, 1907, i, 242; from *Physikal. Zeitsch.*, 1906, **7**, 805).—When an ethereal solution of chloropicrin is mixed with magnesium phenyl bromide, a green flame is formed under the ether, which does not, however, take fire. Diphenyl is the only product which has been isolated from the mixture. E. W. W.

Action of Carbon Dioxide on Magnesium Phenyl Bromide. Georg Schroeter (*Ber.*, 1907, **40**, 1584—1585. Compare Abstr., 1903, i, 821).—Meyer and Tögel (Abstr., 1906, i, 757) confirm the observation of the author that under certain conditions triphenylcarbinol and benzophenone are obtained by the action of carbon dioxide on magnesium phenyl bromide. They conclude that the presence of water or alcohol is necessary and that the temperature must be raised during the action of the carbon dioxide. The author maintains that the presence of water is not necessary. The temperature, however, has an important influence, as well as the rate at which the carbon dioxide is passed into the solution of magnesium phenyl bromide.

When a slow current of dry carbon dioxide is passed into a boiling ethereal solution of magnesium phenyl bromide, the product yields benzoic acid, triphenylcarbinol, benzophenone, and diphenyl. When dry carbon dioxide ($\frac{1}{3}$ mol.) is passed into a cooled ethereal solution of magnesium phenyl bromide (1 mol.), the product yields triphenyl carbinol, benzophenone, and diphenyl, but no benzoic acid. A. McK.

Organic Chemistry.

Origin of Mineral Oil (Artificial Preparation of Optically Active Petroleum). Carl Neuberg (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, **24**, 451—455. Compare Walden, Abstr., 1906, ii, 368). —The fact that many kinds of petroleum from various sources are optically active necessitates a revision of the hypothesis of Engler and Hofer (Abstr., 1888, 928; 1889, 586), since neither fats nor their decomposition products are optically active, and hence cannot give rise to an optically active mineral oil. In continuation of his observation that proteins give rise to optically active fatty acids on decomposition (Abstr., 1906, i, 923), the author has been able to show that by the dry distillation of a mixture of oleic acid and *d*-valeric acid, also by heating such a mixture under pressure, a product is obtained which when purified possesses all the properties of natural petroleum, likewise the same optical rotatory power. Further, the optical rotatory power increases as the boiling point of the fraction increases, and these high boiling fractions give the cholesterol colour reaction (Neuberg, Abstr., 1906, ii, 497), as do the high boiling fractions obtained from natural petroleum.

In conclusion, the author briefly mentions that the acids formed during the putrefaction of cheese frequently do not possess a normal structure as is generally supposed, since besides β-methylbutyric acid and γ-methylvaleric acid, the optically active acids, α-methylbutyric acid and β-methylvaleric acid are also found in putrid cheese. No aminobutyric acid is found in the putrefaction products of casein, so that the butyric acid, which is present to the extent of one-third of the total acids formed, is undoubtedly produced by the decomposition of glutamic acid. It is also very probable that several optically active acids are formed during the putrefaction of gelatin.

W. H. G.

Catalytic Dehydration of Alcohols by Amorphous Phosphorus and Phosphates. Jean B. Senderens (*Compt. rend.*, 1907, **144**, 1109—1111).—In the presence of commercial amorphous phosphorus in the form of an impalpable purple powder, D = 2·165, the alcohols are decomposed at 180° (approx.) into olefine and water together with traces of hydrogen phosphide. Thus ethyl alcohol begins to decompose at 215°, and at 230—240° gives a mixture of 95% of ethylene and 5% of hydrogen phosphide. Propyl alcohol gives similar results, whilst butyl alcohol at 205° gives 97% of butylene and 3% of hydrogen phosphide. All specimens of amorphous phosphorus are, however, not equally active, but it can be replaced by various phosphates, of which aluminium phosphate is the most active and is the basis of a general method for the preparation of open chain and *cyclo*-olefines. Ethyl alcohol begins to decompose at 330° and gives pure ethylene in abundance at 380°. *n*-Propyl alcohol decomposes into propylene and water at 300—340°. *n*-Butyl alcohol at 320° gives 27% of *iso*butylene and 73% of *a*-butylene; *iso*butyl alcohol at 310°, a mixture of 68·5% of *iso*butylene and 31·5% of *a*-butylene. Trimethylcarbinol at 200° gives pure *iso*butylene; *iso*propyl alcohol at 300°, propylene; *iso*amyl alcohol at 300—350°, a mixture of *a*-*iso*amylene and γ-amylene with traces of β-methyl-Δ^{β}-butylene and *a*-amylene; *tert.*-amyl alcohol, β-methyl-Δ^{β}-butylene; *n*-octyl alcohol, *a*-octylene, b. p. 122—123°; and *sec.*-octyl alcohol, an octylene, b. p. 120·5—121·5°. The method is readily applicable to the *cyclo*paraffin alcohols, and theoretical yields of the corresponding *cyclo*-olefines are obtained at 300—350° from *cyclo*hexanol, the three methyl*cyclo*hexanols, 1 : 3 : 4-dimethyl*cyclo*hexanol, and menthol. The silicates have similar, but less powerful, catalytic properties, whilst silica has the singular property of being a dehydrogenating catalyst when in the crystalline condition and a dehydrating catalyst when amorphous.

E. H.

Isomerisation Point of *sec.*- and *tert.*-Pinacolyl Alcohol Derivatives. Maurice Delacre (*Bull. Soc. chim.*, 1907, [iv], 1, 575—586).—In continuation of previous work on the isomerisation of pinacolyl derivatives (Abstr., 1906, i, 477, 518, 551, 784; this vol., i, 459), the author has compared the action of potassium acetate on *sec.*-pinacolyl bromide and the hydrobromide of $\beta\gamma$-dimethyl-Δ^{β}-butylene. The former furnishes 39·3% of the symmetrical hydrocarbons, $CMe_2{:}CMe_2$ and $CHMe_2{\cdot}CMe{:}CH_2$, and a residue, which contains *tert.*-pinacolyl acetate and a bromide, which may be the compound $CMe_3{\cdot}CHMeBr$. The hydrobromide of $\beta\gamma$-dimethyl-Δ^{β}-butylene under the same conditions yields a similar proportion of the two symmetrical hydrocarbons, and the residue is almost wholly composed of *tert.*-pinacolyl acetate. From these results the inferences are drawn that by the action of hydrogen bromide on *sec.*-pinacolyl alcohol about 94% of $CBrMe_2{\cdot}CHMe_2$ and about 6% of the unsymmetrical bromide, $CMe_3{\cdot}CHMeBr$, are formed.

T. A. H.

Synthesis and Decomposition of $\beta\delta$-Dihydroxy-$\beta\gamma\gamma\delta$-tetramethylpentane. A. N. Slavjanoff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 140—160).—The investigation was undertaken with the object of preparing hexamethyl*cyclo*propane by the action of hydrogen bromide on the glycol, which, according to Grignard, should be obtained by the action of magnesium methyliodide on ethyl dimethylacetoacetate (*Ann. Chim. Phys.*, 1901, [vii], **24**, 463). This attempt was, however, not successful, but the glycol, *$\beta\delta$-dihydroxy-$\beta\gamma\gamma\delta$-tetramethylpentane*,

$$CMe_2(CMe_2{\cdot}OH)_2,$$

was isolated and its properties investigated. It forms colourless, feathery crystals, m. p. 76·5°, b. p. 223—225°/753 mm., of burning taste and camphoraceous odour, is sparingly soluble in water and very unstable in the presence of mineral and even dilute organic acids; this probably explains why Grignard, who worked in acid solution, was unable to obtain the substance $CEt_2(CMe_2{\cdot}OH)_2$. *iso*Butyric acid and β-hydroxy-$\alpha\alpha\beta$-trimethylbutyric acid were obtained as by-products in the preparation of the pentane. The same substance is obtained when dimethylmalonic ester is substituted for dimethylacetoacetic, but the yield is less. The products of dehydration of the glycol consist chiefly of acetone and $\beta\gamma$-dimethyl-Δ^{β}-butylene. When treated with phosphorus and bromine, the glycol yields $\beta\gamma$-dibromo-$\beta\gamma$-dimethylbutane. With hydrobromic acid, the mono-bromo-derivative, $CHMe_2\cdot CMe_2Br$, is formed. Z. K.

Friedel's Pinacolin-pinacone and the Constitution of Ordinary Pinacolin. MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 535—543. Compare this vol., i, 459).—When pinacolin is reduced with sodium there is formed in addition to *sec.*-pinacolyl alcohol (methyl-*tert.*-butylcarbinol) a solid product, which Friedel called pinacolin-pinacone; this according to Couturier (Abstr., 1893, i, 245) is decomposed by dilute acids into pinacolin and $\beta\gamma$-dimethyl-Δ^{β}-butylene. This opens up the question as to whether Friedel's pinacolin-pinacone is itself a symmetrical compound or gives rise to a symmetrical hydrocarbon as a decomposition product owing to initial isomerisation.

The author finds that in addition to the two products named, a third *substance*, b. p. 200—225°, is produced when pinacolin is reduced with sodium, but it is not certain that this may not be produced from an impurity in the pinacolin used. Pinacolin-pinacone, b. p. 255—258°, m. p. 71—72°, crystallises from light petroleum. When heated with acetic anhydride in a closed vessel it yields pinacolin and *sec.*-pinacolyl acetate. With acetyl chloride, *sec.*-pinacolyl acetate, and with phosphorus trichloride, *sec.*-pinacolyl chloride is produced, accompanied in each case by a second substance, a liquid *hydrocarbon*, $C_{12}H_{20}$, b. p. 180° (approx.), which has a feeble characteristic odour and readily absorbs bromine.

The formula suggested by Couturier for pinacolin-pinacone affords an explanation of the first of these reactions, thus: $CMe_3\cdot CMe(OH)\cdot CMe(OH)\cdot CMe_3 \longrightarrow CMe_3\cdot CHMe\cdot OH + CMe_3\cdot COMe$, but does not account for the formation of the hydrocarbon $C_{12}H_{20}$. These reactions indicate therefore that pinacolin furnishes unsymmetrical products on reduction with sodium. T. A. H.

Explosive Mixtures of Air and Ethyl Ether. JEAN MEUNIER (*Compt. rend.*, 1907, **144**, 1107—1108. Compare this vol., i, 460).—By the use of smaller containing vessels (190 c.c. and 252 c.c. instead of 1 litre) the author obtains the values of 0·058 gram and 0·059 gram per litre for the lower limit of inflammability of ethyl ether in air, thus agreeing with the value 0·06 gram per litre obtained by Le Chatelier and Boudouard (Abstr., 1898, ii, 574). The higher result previously obtained is probably due to incomplete mixing in the larger vessel. When the proportion of ethyl ether is 0·06 gram per litre, it burns without noise. With a higher proportion, explosion occurs, the explosion being violent between the limits 0·1 and 0·175 gram per litre, and the maximum violence occurring with the proportion 0·12—0·15 gram per litre. As the amount of ethyl ether increases above 0·175 gram per litre, the combustion becomes calmer and ceases with 0·195 gram per litre. Similar results are obtained with carbon disulphide, but in this case the higher limit amounts to 0·9 gram per litre.

E. H.

Compounds of Aluminium Bromide with Ethyl Ether. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 163—167).—In view of the interest which attaches to complex aluminium compounds as well as ethereal compounds in regard to chemical constitution, it seemed desirable to obtain compounds of aluminium bromide with ether by a process which would exclude the formation of any by-products. Quite colourless, freshly distilled aluminium bromide was introduced as a layer in the reacting vessel and absolutely pure; dry ethyl ether was then introduced by means of a capillary reaching to the bottom of the vessel. On evaporating the ether in a vacuum, dry, colourless crystals of the formula $AlBr_3,OEt_2$, m. p. 47°, were obtained. The substance is very unstable and readily soluble in ether, bromine, benzene, &c. Unlike the non-electrolytic solutions of aluminium bromide in the same solvents, the solutions of the complex substance show no evidence of chemical reaction and are electrolytes; it is therefore probable that the aluminium in this compound has formed a complex ion. The experiments also indicate that with the formation of stable, complex ions in the compounds of aluminium, those of its reactions which depend on the formation of complex ions are either considerably weakened or altogether disappear.

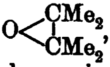
Z. K.

Reaction between Titanium Tetrachloride and Ethyl Ether. HENRY R. ELLIS (*Chem. News*, 1907, **95**, 241).—Anhydrous ethyl ether was added slowly to titanium tetrachloride cooled in ice; reaction took place at once and the mixture ultimately set to a mass of yellow crystals resembling rhombic sulphur. After twenty-four hours, the solid was distilled; the first fraction consisted of ether, hydrogen chloride, and a small quantity of a yellow liquid which crystallised; the second fraction, 34—60°, consisted of a yellow oil which solidified to yellow crystals; the third fraction, 60—100°, was a yellow liquid which solidified to small, yellowish-white crystals; and the last fraction, 170—196°, consisted of orange crystals, m. p. about 70°. The residue, which formed a brown powder resembling hydrated oxides of manganese, was washed with light petroleum and analysed; it contained 34·4% of titanium and 18% of chlorine. The other substances slowly decompose with evolution of hydrogen chloride and ethyl chloride.

P. H.

Methyl Ethers of Allyl- and Propargyl-carbinols. ROBERT LESPIEAU (*Compt. rend.*, 1907, **144**, 1161—1162).—By alternately adding to magnesium covered with dry ether successive small quantities of allyl bromide and methyl chloride, a mixture of diallyl and the ether $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$ is obtained. Complete separation of the latter is impossible by fractional distillation, but is easily effected after conversion into the bromo-derivatives.

The *ether*, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, b. p. 90—91°/13 mm., 101—102°/25 mm., 209—211°/760 mm. (decomp.), D^0 1·811, is converted by hydrogen bromide into γδ-dibromo-*n*-butyl alcohol, is reduced by zinc dust and alcohol to the unsaturated ether $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, and by treatment with sodium ethoxide gives a mixture of the *ether* $CH_2{:}CBr{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, b. p. 142—143°, D^0 1·356, and the *ether* $CHBr{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, b. p. 149—151°, D^0 1·358. Both the latter ethers react with aqueous or alcoholic potash giving the acetylenic *ether* $CH{⋮}C{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, having b. p. 86—87°, D^0 0·8579, and giving a yellow precipitate with ammoniacal cuprous chloride solution. E. H.

Tetramethylethylene [βγ-Dimethyl-Δ^{β}-butylene] Oxide. MAURICE DELACRE (*Bull. Soc. chim.*, 1907, [iv], 1, 586—590).—It has frequently been asserted that the formation of pinacolin, $CMe_3{\cdot}COMe$, from pinacone, $OH{\cdot}CMe_3{\cdot}CMe_2{\cdot}OH$, takes place through the isomerisation of some tetramethylethylene oxide, , first formed, but this transformation has not yet been realised experimentally.

The method recommended by Eltekoff (Abstr., 1883, 567) for the preparation of the oxide does not in the author's experience give good results, and he has used instead that suggested by Friedel, which consists in treating pinacone with dry hydrogen chloride and distilling the product over potassium hydroxide. The rectified distillation product was finally separated into eight fractions. From that boiling at 90—100° a portion boiling at 92·5—99° was isolated. This had a peculiar odour, was partially transformed into pinacone in contact with water, and on reduction with sodium in presence of an aqueous solution of potassium hydroxide yielded some *tert.*-pinacolyl alcohol mixed with the *sec.*-alcohol; the presence of the latter may be due either to isomerisation or to impurities in the liquid reduced. The fraction, b. p. 109—115°, on reduction gave mainly *tert.*-pinacolyl alcohol, and no indication of the occurrence in it of the alcohol $CH_2{:}CMe{\cdot}CMe_2{\cdot}OH$ was obtained. The portion boiling below 90° consisted mainly of hydrocarbons and gave gummy precipitates with hydrobromic acid. The fraction boiling between 90° and 109° gave with this reagent pinacone bromide, $CMe_2Br{\cdot}CMe_2Br$, and with hydrochloric acid an oily product. T. A. H.

New Method of Synthesis of Diprimary Compounds containing an Odd Number of Carbon Atoms: αη-Dimethoxyheptane. JULES L. HAMONET (*Compt. rend.*, 1907, **144**, 1217—1219. Compare Abstr., 1904, i, 467).—The δ-chloro-αη-dimethoxyheptane described previously (Abstr., 1906, i, 58) does not form a magnesium compound, but the chlorine can be replaced by hydrogen by the action of sodium on the ethereal solution containing hydrogen chloride. The resulting *αη-dimethoxyheptane*, $CH_2({\cdot}[CH_2]_3{\cdot}OMe)_2$, is a very mobile liquid, b. p. 189—190°, D^{18} 0·860, having an agreeable fruity odour. The δ-bromo-α-amyloxybutane and ε-bromo-α-amyloxypentane previously described (Abstr., 1904, i, 467, 705) and Dionneau's ζ-bromo- and ζ-iodo-α-ethoxyhexane (Abstr., 1906, i, 134) would, by reacting with ethyl formate, give similar halogen ethers, from which sodium would withdraw the bromine giving diprimary compounds containing C_9, C_{11}, and C_{13} respectively. The method is probably applicable to all the homologues $RO(CH_2)_nBr$. E. H.

Crystalline "Acidates" (Compounds of Magnesium Bromide and Iodide with Organic Acids). BORIS N. MENSCHUTKIN (*Zeitsch. anorg. Chem.*, 1907, **54**, 89—96; *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1335—1346. Compare Abstr., 1906, i, 131, 132; this vol., i, 271).—The compounds in question have been prepared mainly by the action of the anhydrous acids on the dietherates of the salts. In some cases the solubility of the compounds in the corresponding free acids have been determined from 0° to the respective melting points.

The *compounds* $MgBr_2,6CH_2O_2$ (m. p. 88°) and $MgBr_2,6C_2H_4O_2$ (m. p. 112°) occur in colourless, extremely hygroscopic crystals. The solubility curve of the former in formic acid shows no distinct bend, whilst that of the latter in acetic acid rises steeply to about 80°, beyond which point it becomes much flatter, indicating a much more rapid increase of solubility with temperature above the latter point.

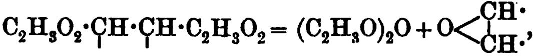
The following compounds with magnesium iodide have been prepared: $MgI_2,6C_2H_4O_2$, m. p. 142°; $MgI_2,6C_3H_6O_2$, m. p. 55—56°, and $MgI_2,6C_4H_8O_2$, m. p. 68°. The solubility curve of the acetic acid compound has the same form as that of the corresponding compound with magnesium bromide. The compounds with formic and valeric acids could not be obtained in crystalline form.

The compounds with calcium chloride, referred to in the latter part of the paper, have been described previously (this vol., i, 272). G. S.

Interaction of Olein and Mercuric Acetate in Acetic Acid. ALEXANDRE LEYS (*Bull. Soc. chim.*, 1907, [iv], 1, 543—548. Compare Abstr., 1905, i, 433, ii, 655; this vol., i, 379).—As the result of determinations of the amount of mercurous acetate formed in the interaction of olein or fats containing unsaturated acids, with mercuric acetate, in presence of acetic acid, under the conditions already described (this vol., i, 379), the author suggests that the principal reaction may be regarded as taking place in the following way:

$$\cdot CH{:}CH\cdot + 2Hg(C_2H_3O_2)_2 = C_2H_3O_2\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot C_2H_3O_2 + Hg_2(C_2H_3O_2)_2.$$

The diacetate so formed is decomposed to some extent by the boiling acetic acid in accordance with the following equation:

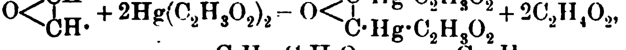


$$C_2H_3O_2\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot C_2H_3O_2 = (C_2H_3O)_2O + O<\begin{matrix}CH\cdot\\ |\\ CH\cdot\end{matrix},$$

and it is to this reaction that the noticeable browning of the liquid is due.

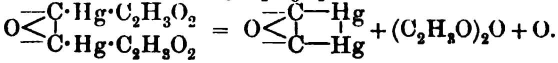
The eventual fixation of some mercury is explained by reactions represented as follows:

(1)



$$O<\begin{matrix}CH\cdot\\ |\\ CH\cdot\end{matrix} + 2Hg(C_2H_3O_2)_2 = O<\begin{matrix}-C\cdot Hg\cdot C_2H_3O_2\\ |\\ C\cdot Hg\cdot C_2H_3O_2\end{matrix} + 2C_2H_4O_2,$$

(2)

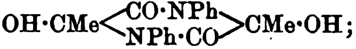


$$O\begin{matrix}=\\ <\\ =\end{matrix}\begin{matrix}C\cdot Hg\cdot C_2H_3O_2\\ |\\ C\cdot Hg\cdot C_2H_3O_2\end{matrix} = O\begin{matrix}=\\ <\\ =\end{matrix}\begin{matrix}C-Hg\\ |\quad\;\, |\\ C-Hg\end{matrix} + (C_2H_3O)_2O + O.$$

The mercurialised groups in the two chief products of these reactions, by the action of the oxygen set free in the second reaction, may be transformed into ·CO·CO· with the liberation of mercurous acetate and mercury respectively. T. A. H.

Transformation of the Esters of α-Bromo-Fatty Acids into Esters of α-Iodo-Fatty Acids. F. BODROUX and FÉLIX TABOURY (*Compt. rend.*, 1907, **144**, 1216—1217. Compare Bodroux, Abstr., 1905, i, 585).—On adding the ester of an α-bromo-fatty acid to an ethereal solution of magnesium iodide, obtained by treating magnesium turnings with iodine in presence of excess of ether, an energetic reaction takes place and the corresponding iodo-ester is formed in an almost theoretical yield. In this manner, ethyl bromoacetate is converted into ethyl iodoacetate, a liquid, b. p. 85—86°/25 mm., D^{24} 1·762; ethyl α-bromopropionate into *ethyl α-iodopropionate*, a liquid, b. p. 85°/38 mm., D^{17} 1·662, and ethyl α-bromobutyrate into ethyl α-iodobutyrate, a liquid with b. p. 100—101°/21 mm., D^{17} 1·570. These three esters emit irritating vapours at the ordinary temperature, and are decomposed rapidly by heat and light with liberation of iodine. E. H.

Amides of Pyruvic Acid. ALFRED WOHL and L. H. LIPS (*Ber.*, 1907, **40**, 2312—2315).—It is shown that the methylanilide and the diethylamide of pyruvic acid are stable and do not tend to polymerise in the same manner as the anilide (Nef, Abstr., 1892, 1441; Bischoff and Walden, *ibid.*, 1893, i, 511), thus indicating that it is the hydrogen atom attached to nitrogen which takes part in the polymerisation. The formula suggested for the bimolecular anilide is



$$\mathrm{OH\cdot CMe}<\begin{matrix}\mathrm{CO\cdot NPh}\\ \mathrm{NPh\cdot CO}\end{matrix}>\mathrm{CMe\cdot OH};$$

it forms a sodium derivative with two equivalents of sodium hydroxide.

The crude *methylanilide*, $C_{10}H_{11}O_2N$, after extraction with concentrated hydrochloric acid solidifies and then crystallises from water in snow-white needles, m. p. 152—153°. The *diethylamide*, $C_7H_{18}O_2N$, is an oil, b. p. 100°/18·3 mm., and dissolves readily in cold water, but separates when the solution is warmed or is made strongly alkaline.

J. J. S.

Hydroxyfumaric and Hydroxymaleic Acids. ALFRED WOHL (*Ber.*, 1907, **40**, 2282—2293. Compare Wohl and Oesterlin, Abstr., 1901, i, 365; Michael, Abstr., 1906, i, 179; Michael and Bucher, *ibid.*, 1896, i, 599).—Both acids in alcoholic solution readily yield intense colorations with ferric chloride and both are readily oxidised by permanganate. The properties described in the following abstracts are in harmony with the enolic nature of the two acids. The readiness with which the one form is transformed into the other, when compared with other examples of cis-trans isomerism, may be accounted for by the intermediate formation of the ketonic form. The salts are probably derived from the ketonic form, as they differ considerably from the acids as regards stability. All the salts when acidified yield the acid of lower m. p. Hydroxymaleic acid decomposes at 152° (not 146° as previously given) and hydroxyfumaric acid at 184°.

J. J. S.

Oxalacetic Acid. ALFRED WOHL and CARL H. LIPS (*Ber.*, 1907, 40, 2294—2300).—Hydroxymaleic acid is formed when the pyridine salt of hydroxymaleic anhydride (Wohl and Oesterlin, Abstr., 1901, i, 365) is decomposed with 12% sulphuric acid, and hydroxyfumaric when 30% acid is used. *Dibenzylamine hydroxymaleate*, $C_{18}H_{19}O_5N$, is obtained when absolute alcoholic solutions of the base and of hydroxyfumaric acid are mixed. It crystallises from acetone, but is insoluble in cold alcohol; m. p. 127—128° (decomp.). When decomposed with hydrochloric acid, it yields hydroxymaleic acid, and the same salt is formed by the union of dibenzylamine and hydroxymaleic acid.

Hydroxymaleinanilic acid, $CO_2H{\cdot}CH{:}C(OH){\cdot}CO{\cdot}NHPh$, is obtained by the addition of an excess of an absolute alcoholic solution of aniline to the pyridine salt at -20° to -15°, and is isolated by the addition of 5*N*-hydrochloric acid. It crystallises from benzene in snow-white crystals, m. p. 112—113° (decomp.). The *sodium* salt has m. p. 156—158° (decomp.), and dissolves sparingly in absolute alcohol, and also in water (20 parts) at 22°. *Hydroxyfumaranilic acid*, $C_{10}H_9O_4N$, is obtained in a similar manner from the pyridine salt, but using 10*N*-sulphuric acid and extracting with ether. It crystallises from benzene and has m. p. 141—142° (decomp.). The two isomerides may be transformed each into other. The addition of 10*N*-sulphuric acid to an alcoholic ethereal solution of the maleic derivative at -20° converts it into the fumaric, and the addition of 5*N*-hydrochloric acid to the aniline salt of the fumaric compound at -20° yields the maleinanilic acid.

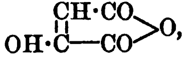
In the presence of aniline the alcoholic solutions of the two acids are unstable, and even at -13° begin to evolve carbon dioxide.

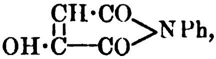
Dibenzylamine reacts with the pyridine salt in alcoholic solution at 60—70°, yielding *hydroxymaleindibenzylamic acid*,

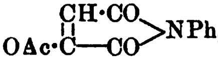
$$CO_2H{\cdot}CH{:}C(OH){\cdot}CO{\cdot}N(CH_2Ph)_2,$$

which separates from benzene in colourless crystals, m. p. 147° (decomp.).

J. J. S.

Anhydride and Anil of Hydroxymaleic Acid. ALFRED WOHL and W. FREUND (*Ber.*, 1907, 40, 2300—2308).—*Hydroxymaleic anhydride*,  $\left.\begin{array}{l}CH{\cdot}CO\\ \;\|\\ OH{\cdot}C{-}CO\end{array}\right>O$, may be obtained by the action of hydrogen chloride on an absolute ethereal solution of its pyridine salt provided moisture is rigorously excluded during all the operations, namely, shaking, filtration, and removal of the ether. It separates from its chloroform solution on the addition of light petroleum in the form of yellow needles. When heated in a closed capillary tube it decomposes at 82—83° (corr.), yielding a solid which melts and decomposes at 120°.

Hydroxymaleic acid anil,  $\left.\begin{array}{l}CH{\cdot}CO\\ \;\|\\ OH{\cdot}C{-}CO\end{array}\right>NPh$, is obtained by the action of acetyl chloride on the anilic acid (preceding abstract) at 40—43°. When pure it is quite white, but in the presence of moisture turns yellow, owing to the formation of an anhydride, the same decomposition occurs rapidly when the anil is heated at 120°. Aniline transforms the anil into anilinomaleic acid anil.

Acetoxymaleic acid anil,  $\overset{CH\cdot CO}{\underset{OAc\cdot C—CO}{\|}}\!>NPh$, obtained together with xanthoxalanil (Ruhemann, Trans., 1906, **89**, 1236, 1847) by the action of acetyl chloride or acetic anhydride and sulphuric acid on hydroxymaleinanilic acid, crystallises from carbon disulphide, and has m. p. 125°. The yellow xanthoxalanil is transformed into a red modification when rubbed or heated, and this modification yields the yellow compound when crystallised from glacial acetic acid. When heated with aniline on the water-bath, the xanthoxalanil yields *anilinodimaleic acid anil,* $C_{26}H_{17}O_4N_3$, which decomposes above 260°.

Hydroxymalein-p-*tolilic acid,* $C_{11}H_{11}O_4N$, begins to decompose at 99° when slowly heated or melts and decomposes at 114° when rapidly heated. The p-*tolil,* $C_{11}H_9O_3N$, is more stable in moist air than the anil, but when heated at 160° yields the anhydride, *xanthoxaltolil,* $C_{22}H_{16}O_5N$, which exists in yellow and red modifications, m. p. 263—264° (decomp., corr.).

p-*Toluidinoacryl*-p-*toluidide,* $C_{17}H_{18}ON_2$, crystallises from alcohol in colourless needles, m. p. 150°, and dissolves readily in ether, benzene, acetone, or water. The p-*toluidide* of pyruvic acid,

$$CH_3\cdot CO\cdot CO\cdot NH\cdot C_6H_4Me,$$

has m. p. 109°. J. J. S.

[Constants of] Hydroxymaleic and Hydroxyfumaric Acid.

ALFRED WOHL and P. CLAUSSNER (*Ber.*, 1907, **40**, 2308—2312).—A modification of Wohl and Oesterlin's method (Abstr., 1901, i, 365) for the preparation of hydroxyfumaric acid is described. The following physical constants for the isomeric acids have been determined:

	Hydroxymaleic.	Hydroxyfumaric.
Molecular heat of combustion at constant volume	286·58 Cal.	275·78 Cal.
Heat of formation calc.	230·3 „	241·1 „
Dissociation constant *K*	0·2505	0·276
Molecular refraction in propyl alcoholic solution:		
D line	24·90	25·32
C „	24·90	25·21
F „	25·35	25·35
Do. in aqueous solution:		
D line	23·90	23·94
C „	24·28	24·35

These values agree fairly well with those required for the enolic form of oxalacetic acid. J. J. S.

Partial Racemism. VI. ALBERT LADENBURG and LEO FISCHL (*Ber.*, 1907, **40**, 2279—2281. Compare Abstr., 1903, i, 575).—When a solution containing molecular proportions of brucine and racemic acid is crystallised from water below 50°, a crystalline salt is obtained, $C_{23}H_{26}O_4N_2,C_4H_6O_6,2\frac{1}{2}H_2O$, and the acid obtained from this is optically inactive. It is the partially racemic acid salt, brucine hydrogen racemate. When the crystals separate at a temperature above 50°, they have quite a different appearance, and the recovered acid is lævorotatory. According to Pasteur, the *l*-tartrate contains $5H_2O$, whereas the *d*-tartrate is anhydrous. That the crystals separating at the lower temperature are not a mere mixture of the *d*- and *l*-acid tartrates has been shown by sp. gr. and solubility determinations.

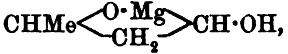
100 parts of water dissolve at

	20°.	25°.	35°.	44°.	56°.
Tartrate mixture	1·986	2·177	2·860	3·628	4·638
Racemate	1·411	1·638	2·539	3·629	4·983

The two curves cut at 44°, and at this temperature the solubility of the racemate is not affected by the addition of an excess of *d*- or *l*-tartrate. In neutral solution, racemic acid is not resolved at the ordinary temperature by brucine. The racemate has the composition $(C_{22}H_{26}O_4N_2)_2,C_4H_6O_6,9H_2O$, and is not resolved at temperatures up to 100°. J. J. S.

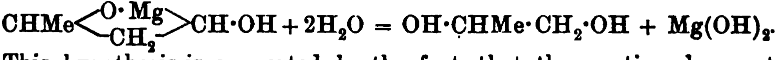
Ethylthioglycollic [Ethylthiolacetic] Acid. LUDWIG RAMBERG (*Ber.*, 1907, **40**, 2588—2589. Compare Klason, *Ber.*, 1875, **8**, 121). —Ethylthiolacetic acid is obtained quantitatively from sodium mercaptide and sodium chloroacetate in concentrated aqueous solution, the acid being liberated by the addition of excess of sulphuric acid. It has b. p. 164°/83 mm. and 117—118°/11 mm., m. p. $-8·7°$, D_{20}^{20} 1·1518, and D_4^{20} 1·1497. The value *K* is 0·0183. C. S.

Action of Magnesium Amalgam on Aldehydes. ANDRÉ KLING and PAUL ROY (*Compt. rend.*, 1907, **144**, 1111—1114. Compare L. Meunier, Abstr., 1902, i, 335).—Magnesium amalgam acts on aliphatic aldehydes producing the aldol condensation, followed by a reduction of the aldol formed. In presence of the amalgam, the aldehyde seems to act in the two desmotropic forms $CH_3·CHO$ and $CH_2:CH·OH$, forming the complex compound



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{O\cdot Mg}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot OH},$$

which is decomposed by water, thus:



$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{O\cdot Mg}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH\cdot OH} + 2H_2O = \mathrm{OH\cdot CHMe\cdot CH_2\cdot OH} + \mathrm{Mg(OH)_2}.$$

This hypothesis is supported by the fact that the reaction does not take place when (as with chloral) tautomerism from the $R·CH_2·CHO$ to the $R·CH:CH·OH$ form is impossible.

Trioxymethylene does not react with magnesium amalgam. Acetaldehyde reacts very violently, giving a 15% yield of a glycol, $C_4H_{10}O_2$, b. p. 203—204°, which Meunier considered to be βγ-butanediol, but which the authors by a differentiation method previously described (Kling and Viard, Abstr., 1904, i, 545) have decided is the glycol $OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH$. Propaldehyde gives a mixture of Talberg's β-methylpentane-αγ-diol,

$$CH_2Me\cdot CH_2\cdot CH(OH)\cdot CHMe\cdot CH_2\cdot OH,$$

and its propionic ester. From benzaldehyde, magnesium and benzyl benzoate and a small quantity of *iso*hydrobenzoin are obtained.

E. H.

Nonaldehyde Semicarbazone. CARL HARRIES and HANS O. TÜRK (*Ber.*, 1907, **40**, 2756).—Bagard (this vol., i, 384) finds the semicarbazone of synthetic nonaldehyde to melt at 100°, whereas the authors (this vol., i, 11) found that from oleic acid ozonide to have m. p. 84°. They now find that if the nonaldehyde be purified previously by means of the sodium bisulphite compound, the semicarbazone has m. p. 100°. E. F. A.

Chemical Action of Light. XI. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1907, **40**, 2415—2424. Compare Abstr., 1906, i, 10).—It has been shown (Abstr., 1903, i, 562) that acetone in aqueous solution under the influence of sunlight is hydrolysed with the formation of acetic acid and methane. The present investigation was undertaken with the object of ascertaining whether other ketones in solution are similarly affected by sunlight. It is found that in aqueous solution, methyl ethyl ketone is hydrolysed into acetic acid and ethane, whilst lævulic acid yields propionic acid and in all probability also formic acid and methyl alcohol, but not acetic acid. Lævulic acid in alcoholic solution is probably converted into its ethyl ester and partially into γ-hydroxyvaleric acid, the formation of which is accompanied by the oxidation of part of the alcohol to acetaldehyde. Menthone, dissolved in dilute alcohol, yields decoic acid and an aldehyde, which is probably identical with Wallach's menthocitronellaldehyde (Abstr., 1897, i, 427). W. H. G.

Dihydroxytetramethylacetone. LOUIS HENRY (*Compt. rend.*, 1907, **144**, 1200—1202).—By the action of magnesium methyl bromide (5 mols.) on ethyl mesoxalate (1 mol.), *dihydroxytetramethylacetone*, $CO(CMe_2\cdot OH)_2$, is formed, although the carbonyl group is more readily attacked by organo-magnesium compounds than is the carbethoxy-group, and sufficient magnesium methyl bromide is used to react with all three groups. Dihydroxytetramethylacetone forms white needles, m. p. 117—118°, b. p. 238—240°. The differences between its melting and boiling points and those of pinacone are very nearly the same as those between glycol and αγ-dihydroxyacetone and between βγ-dimethylbutane (di*iso*propyl) and di*iso*propyl ketone respectively.

E. H.

Direct Hydrogenation of Aliphatic Diketones. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1907, **144**, 1086—1089. Compare Sabatier and Senderens, Abstr., 1903, i, 733; Darzens, Abstr., 1905, i, 66).—When diacetyl is submitted to hydrogenation in presence of reduced nickel at 140—150°, it is completely transformed into a mixture of almost equal volumes of Pechmann's dimethylketol, $OH\cdot CHMe\cdot COMe$ (Abstr., 1890, 1234), and $\beta\gamma$-butanediol,

$$OH\cdot CHMe\cdot CHMe\cdot OH$$

(Eltekoff). Acetylacetone when similarly hydrogenated at 150° gives a mixture of acetaldehyde, acetone, ethyl alcohol, *iso*propyl alcohol, and Claisen's β-hydroxy-δ-ketopentane, $OH\cdot CHMe\cdot CH_2\cdot COMe$ (Abstr., 1899, i, 667). The latter, which has D_0^{15} 0·9677, n_D^{15} 1·4292, is formed to an extent corresponding with one-quarter of the acetylacetone used. Thus three-quarters of the acetylacetone are decomposed according to the reaction $COMe\cdot CH_2\cdot COMe + H_2 = MeCHO + COMe_2$, the acetaldehyde and acetone partially undergoing subsequent hydrogenation to ethyl and *iso*propyl alcohols, whilst the remaining quarter undergoes the normal reaction. The latter reaction occurs less and less as the temperature is raised. In the case of methylacetylacetone,

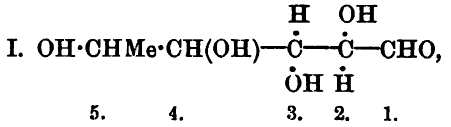
$$CHMe(COMe)_2,$$

hydrogenation at 170° proceeds almost entirely according to a reaction analogous to the first above, the products being acetaldehyde, ethyl alcohol, methyl ethyl ketone, *iso*butyl alcohol, and a very small quantity of a liquid boiling above 190°. Acetonylacetone, when hydrogenated at 190°, is completely converted into water, $\beta\epsilon$-hexylene oxide, $\left.\begin{matrix}CH_2\cdot CHMe\\ |\\ CH_2\cdot CHMe\end{matrix}\right>O$ (compare Béhal, Abstr., 1889, 839), having D_0^{17} 0·833, n_D^{17} 1·4051, and a small quantity of *iso*propyl alcohol. In this case the change proceeds according to the normal reaction, giving $\beta\delta$-dihydroxyhexane, $OH\cdot CHMe\cdot[CH_2]_2\cdot CHMe\cdot OH$, of which the greater proportion is dehydrated, forming water and hexylene oxide, whilst a small quantity is further hydrogenated to *iso*propyl alcohol. E. H.

Fucose. WILLY MAYER and BERNHARD TOLLENS (*Ber.*, 1907, 40, 2434—2440. Compare Abstr., 1905, i, 746).—With the object of ascertaining the configuration of fucose, the products obtained by the oxidation of fucose and fucohexonic acid have been investigated. Fucose when oxidised with nitric acid does not yield mucic acid, but a trihydroxyglutaric acid which seems to be identical with that obtained by Ruff (Abstr., 1899, i, 324) by the oxidation of *d*-arabinose. Fucohexonic acid, prepared by the addition of hydrocyanic acid to fucose and subsequent hydrolysis, was obtained only in the form of its *lactone*, $C_7H_{12}O_6$, crystallising from alcohol in white plates, m. p. 160°, which gave $[\alpha]_D$ +33·3° eight days after the solution had been prepared.

The *barium*, *calcium*, and *cadmium* salts of the acid have been prepared, likewise the *phenylhydrazone*, $C_{13}H_{20}O_6N_2$, which forms rhombic leaflets, m. p. 218°. When oxidised with nitric acid, fucohexonic acid yields oxalic acid and other acids which have not been identified, but no mucic acid, from which it follows that the two hydroxyl

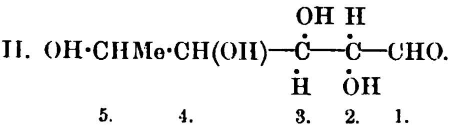
I.



$$OH\cdot CHMe\cdot CH(OH)-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-CHO,$$

5. 4. 3. 2. 1.

II.

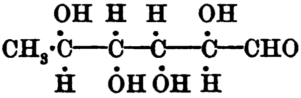


$$OH\cdot CHMe\cdot CH(OH)-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}-CHO.$$

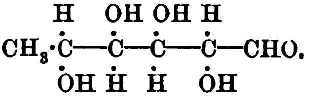
5. 4. 3. 2. 1.

groups attached to the two carbon atoms nearest the aldehyde group in fucose must be situated on opposite sides of the molecule as in I or II.

If now the hydroxyl group attached to carbon atom 4 be situated on the same side as that attached to carbon atom 3, then fucose would possess the configuration present either in *d*- or *l*-arabinose, but the trihydroxyglutaric acid obtained by the oxidation of fucose is undoubtedly identical with that obtained by the oxidation of *d*-arabinose, so that formula I is more probable than formula II. The hydroxyl group attached to carbon atom 5 is probably situated on the opposite side to that on which the hydroxyl group attached to carbon atom 4 is situated, so that fucose would have the formula III. This is quite analogous to the formula assigned to *l*-galactose, and that the two compounds possess a similar structure is highly probable, since the specific rotatory power of fucose is – 75·5°, whilst that of *l*-galactose is – 81°. Since rhodeose is the optical isomeride of fucose (Müther and Tollens, Abstr., 1904, i, 226), it follows that it must possess the formula IV:

III. 

$$CH_3\cdot\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-CHO$$

IV. 

$$CH_3\cdot\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-CHO.$$

W. H. G.

Nature and Structure of Starch. E. Jentys (*Bull. Acad. Sci. Cracow*, 1907, 203—252).—The starch grains occurring in potato, rice, wheat, and sorghum are not homogeneous, but consist of a mixture of colloids composed of reducing sugars and aromatic substances related to the tannins, and glucosidic in character. The stratified starch grains occurring in chloroplastids, leucoplastids, &c., are of different composition at various parts. Stratification is the result of separation from a liquid mixture of carbohydrates and tannin-like substances. The coloration of starch by iodine is due to the presence of aromatic substances, of which one gives a blue tint, another red, a third yellow, and the characteristic colour reactions with iodine usually ascribed to the various dextrins are due to the gradual decomposition of these compounds by diastase, the compound which gives the blue colour disappearing before that giving the red colour, and so on. Sorghum and other starches, which give a red coloration with iodine, differ only from ordinary starch in containing more tannin-like substances which give a red colour with iodine.

The conversion of starch into sugar is not a hydrolytic process, but consists in a separation of reducing sugars from aromatic substances. In the action of enzymes on starch the aromatic substances are probably merely separated, but in the action of acids they are decomposed.

T. A. H.

Crystallography of Halogen Salts of Aliphatic Ammonium Bases. L. Wagner (*Zeitsch. Kryst. Min.*, 1907, **43**, 148—201).—Crystallographic descriptions are given of each of the two dimorphous modifications of the chlorides, bromides, and iodides of the primary, secondary, tertiary, and quaternary methyl- and ethyl-amines. Their morphotropic relations are compared with regard to their topic axes.

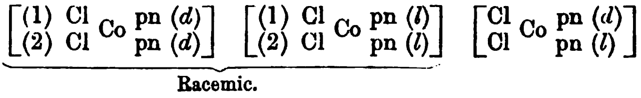
L. J. S.

Substituted Mercurammonium Compounds. K. W. Charitschkoff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**,.230—240).—These compounds were prepared by adding Nessler solution to alkaline solutions of the pure amines. *Mercuriodomethylamine* is formed when the experiment is conducted in the cold, but if the solution is heated the precipitate changes from lemon-yellow to yellow, and has the constitution $IHg\cdot NHMe$. By analogy with these two compounds it is considered that the substance to which Buisson (Abstr., 1906, ii, 704) gives the formula $Hg_9N_4I_6$ is really a mixture of two definite compounds, the proportions of which depend on the conditions of the experiment. *Mercuriodoethylamine*, possibly $HgI_2,Hg_2(NHEt)_2$, is fairly stable when pure. *Mercuriodopropylamine* yields colloidal solutions, and is quite different from any of the other mercurammonium compounds; it can probably be represented as $HgI\cdot Hg\cdot Hg\cdot NI\cdot NHPr,12H_2O$. *Mercuriododiethylamine* separates after a time as a white, crystalline, very unstable substance. Z. K.

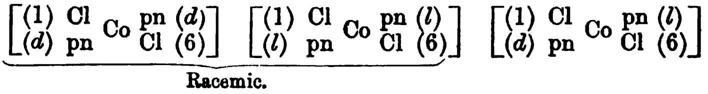
Stereoisomeric Dichlorodipropylenediamine Cobalt Salts. Alfred Werner and A. Fröhlich (*Ber.*, 1907, **40**, 2225—2235).—The stereoisomeric *cis*- and *trans*-dichlorodipropylenediamine cobalt salts of the type $[Cl_2Copn_2]X$ are described $[pn = C_8H_6(NH_2)_2]$, the corresponding salts derived from ethylenediamine already having been described. Since, however, propylenediamine,

$$CHMe(NH_2)\cdot CH_2\cdot NH_2,$$

as distinct from ethylenediamine, contains an asymmetric carbon atom, a new aspect is introduced, and for the complete elucidation of the phenomena of isomerism in this field a considerable amount of further experimental data will be required. The following combinations are possible for the group $[Cl_2Copn_2]$, namely:



$$\underbrace{\left[\begin{matrix}(1)\ \mathrm{Cl}\\(2)\ \mathrm{Cl}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{pn}\ (d)\\\mathrm{pn}\ (d)\end{matrix}\right]\ \left[\begin{matrix}(1)\ \mathrm{Cl}\\(2)\ \mathrm{Cl}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{pn}\ (l)\\\mathrm{pn}\ (l)\end{matrix}\right]}_{\text{Racemic.}}\ \left[\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{pn}\ (d)\\\mathrm{pn}\ (l)\end{matrix}\right]$$



$$\underbrace{\left[\begin{matrix}(1)\ \mathrm{Cl}\\(d)\ \mathrm{pn}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{pn}\ (d)\\\mathrm{Cl}\ (6)\end{matrix}\right]\ \left[\begin{matrix}(1)\ \mathrm{Cl}\\(l)\ \mathrm{pn}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{pn}\ (l)\\\mathrm{Cl}\ (6)\end{matrix}\right]}_{\text{Racemic.}}\ \left[\begin{matrix}(1)\ \mathrm{Cl}\\(d)\ \mathrm{pn}\end{matrix}\ \mathrm{Co}\ \begin{matrix}\mathrm{pn}\ (l)\\\mathrm{Cl}\ (6)\end{matrix}\right]$$

An additional factor, which still further increases the possibilities of isomerism, lies in the unsymmetrical constitution of propylenediamine itself.

The authors predict the possible existence of four inactive praseo-salts of the type in question, and six inactive violeo-isomerides. Of these, two praseo-salts and three violeo-salts should be resolvable into optically active components.

Of these possible isomerides, the authors, so far, have obtained only one praseo- (*trans*-) salt and one violeo- (*cis*-) salt. These compounds, like the corresponding ethylenediamine compounds, are intensely green, but are much more soluble; the chemical behaviour is similar.

An aqueous solution of propylenediamine hydrochloride was gradually added to an aqueous solution of cobalt chloride and the mixture oxidised by passing air through it. Hydrochloric acid was then added, and, after twenty-four hours, trans-*dichlorodipropylenediamine acid chloride*, $[Cl_2\ Co\ pn_2]Cl,HCl,2H_2O$, separated as dark green, rhombic plates. When heated at 105°, the *trans*-salt loses water, and is converted into the isomeric violeo-chloride.

The trans-*chloride*, $[Cl_2\ Co\ pn_2]Cl$, obtained by dissolving the preceding compound in 95% alcohol and then adding ether, separates in bright green leaflets. Its aqueous solution is green, but after some hours becomes pink, probably owing to the formation of the aquo-compound. When the aqueous solution is heated, it assumes a carmine-red colour, and, when evaporated on the water-bath, gives the violet violeo-salt. The action of various acids and of a large number of salts on the chloride in question is described.

The *bromide*, $[Cl_2Copn_2]Br,H_2O$, obtained by the addition of potassium bromide to the preceding chloride, is a pale green, crystalline powder. It cannot be purified by recrystallisation from water, since its aqueous solution on heating is converted into the aquo-salt. The *iodide*, $[Cl_2Copn_2]I$, is yellowish-green and very unstable. The *nitrate*, $[Cl_2Copn_2]NO_3,H_2O$, obtained by the addition of potassium nitrate to the chloride, forms pale green crystals. The *thiocyanate*, $[Cl_2Copn_2]SCN$, is pale green. The *dithionate*, $[Cl_2Copn_2]S_2O_6$, forms glistening, green needles. The *permanganate*, $[Cl_2Copn_2]MnO_4$, has the colour of potassium permanganate. The *hydrogen sulphate*, $[Cl_2Copn_2]SO_4H$, obtained by addition of not too much sulphuric acid to the chloride, separates in green needles and forms a *silver* salt, $([Cl_2Copn_2]SO_4Ag)_2,AgNO_3$, which crystallises in malachite-green, glistening scales. The *platinichloride*, $[Cl_2Copn_2]_2PtCl_6$, obtained by the addition of platinic chloride to the chloride, forms dark green, hexagonal prisms. The *platinosochloride*, $[Cl_2Copn_2]_2PtCl_4$, obtained by the addition of potassium platinosochloride to the chloride, is a pale green, microcrystalline powder. The *aurichloride*, $[Cl_2COpn_2]AuCl_4$, forms grass-green needles. The *mercury chloride* compound,

$$[Cl_2Copn_2]_3Cl_3(HgCl_2)_3,$$

forms green rhoms, needles, or scales. The *ferricyanide*,

$$[Cl_2Copn_2]Fe(CN)_6,$$

is a green powder.

cis-*Dichlorodipropylenediaminecobalt chloride*, $[Cl_2Copn_2]Cl$, obtained either from the acid or neutral praseo-chlorides already described by heating at 105°, is a violet powder. Its aqueous solution is dark violet, but gradually assumes a violet-red tint owing to the formation of aquo-salt. The action on the *cis*-salt of various acids and salts is described. The *dithionate*, $[Cl_2Coen_2]S_2O_6$, prepared by the addition of sodium dithionate to the violeo-chloride, forms green crystals; some dithionate of the aquo-series separates in red crystals at the same time.

A. McK.

Action of Nitrous Acid on Pentamethylenediamine. NIKOLAUS J. DEMJANOFF and M. DOJARENKO (*Ber.*, 1907, **40**, 2589—2594).—This reaction has been studied by Gustavson and Demjanoff (compare Abstr., 1889, 950) and Demjanoff (Abstr., 1894, i, 500), but in consequence of Haworth and Perkin's statement that compounds are produced containing four atoms of carbon (compare Trans., 1894, **65**, 95), the experiments have been repeated. The decomposition of the pentamethylenediamine and the isolation of the products in the form of bromides, alcohols, and glycols have been performed as in the earlier papers. Two bromides of the composition $C_5H_8Br_4$ have been obtained in the crystalline state, with m. p. 86° and 112·5—113° respectively, but the quantities were too small for further investigation. Since, however, $\alpha:\omega$-dichloro- or di-iodo-pentanes and alcoholic potassium hydroxide yield a hydrocarbon, the bromide of which has m. p. 86° and appears to be identical with one of the preceding bromides, the authors conclude that the latter is the tetrabromide of divinylmethane; the other bromide, m. p. 112·5—113°, appears to be piperylene tetrabromide.

The alcohols were fractionally distilled, and the main fraction, b. p. 130—136°, consists of a mixture of Δ^{δ}-penten-α-ol and Δ^{γ}-penten-α-ol; by oxidation with potassium permanganate, formic, acetic, oxalic, and succinic acids are obtained.

The main fractions of the glycols have b. p. 225—230° and 234—236° respectively, and the composition $C_5H_{12}O_2$. They consist of a mixture of pentan-$\alpha\epsilon$-diol and pentan-$\alpha\delta$-diol; this was proved by converting the first-mentioned fraction through the bromide into the nitrile, which by hydrolysis yielded pimelic acid and a small quantity of another acid, which is apparently α-methyladipic acid.

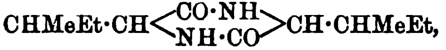
C. S.

Natural Isomeride of Leucine. II. Constitution and Synthesis of *iso*Leucine (α-Amino-β-methylvaleric Acid). FELIX EHRLICH (*Ber.*, 1907, **40**, 2538—2562. Compare Abstr., 1904, i, 560).—The approximate separation of *iso*leucine from valine (compare Fischer, Matsubara, and Hilpert, Abstr., 1906, i, 561) when, as is often the case, the latter is present in considerable quantity, may be effected by heating the mixture with barium hydroxide solution under pressure, preparing the copper salts, and either shaking with cold methyl alcohol or boiling with ethyl alcohol; the copper salt of *iso*leucine dissolves, whilst the other is insoluble.

On dry distillation, *d-iso*leucine yields: (1) partially racemised *d*-amylamine, identical with that prepared by Marckwald (Abstr., 1904, i, 362) from *d*-amyl alcohol; its *platinichloride*,

$$(C_5H_{13}N)_2,H_2PtCl_6,$$

forms golden-yellow, rhombic plates decomposing at 240°; its *sulphate*, $(C_5H_{13}N)_2,H_2SO_4$, decomposes at about 295°. (2) iso*Leucinimide* (iso-2 : 5-*diketo*-3 : 6-*di*iso*butylpiperazine*),



$$\mathrm{CHMeEt{\cdot}CH}\!<\!\begin{matrix}\mathrm{CO{\cdot}NH}\\ \mathrm{NH{\cdot}CO}\end{matrix}\!>\!\mathrm{CH{\cdot}CHMeEt},$$

which separates from alcohol in spherical aggregates of slender, colourless needles, m. p. 280—281°, and has the normal molecular weight in boiling alcohol. This compound has a slight dextrorotation in alcoholic solution, and probably consists of a mixture of several of the four possible stereoisomerides. From these results and the observation that the phenylcarbimide derivative of *iso*leucine yields a hydantoin compound (compare Abstr., 1904, i, 362), the conclusion is drawn that *iso*leucine is an amino-acid containing two asymmetric carbon atoms, and is identical with one of the four possible optically active α-amino-β-methylvaleric acids, $CHMeEt\cdot CH(NH_2)\cdot CO_2H$. This constitution is supported by fermenting sugar in presence of *iso*leucine, the latter being converted into *d*-amyl alcohol (compare Ehrlich, this vol., i, 383) which, on oxidation, yields the dextrorotatory α-methylbutyric acid, $CHMeEt\cdot CO_2H$. Further proof is afforded by the synthesis of *iso*leucine (see also Bouveault and Locquin, Abstr., 1905, i, 636) from *d*-amyl alcohol by oxidising to *d*-valeraldehyde, converting the latter into aminovaleronitrile by the action of hydrogen cyanide and ammonia, and hydrolysing the nitrile. In this way is obtained a mixture of about equal proportions of *iso*leucine and the stereoisomeric alloiso*leucine*. An almost identical mixture is obtained by the action of barium hydroxide solution on natural *d-iso*leucine under pressure, so that *alloiso*leucine must differ from *iso*leucine only in the space-arrangement of the $CO_2H\cdot \overset{*}{C}H\cdot NH_2$ part of the molecule (compare Fischer, this vol., i, 192).

*alloiso*Leucine strongly resembles *iso*leucine in external appearance and in the properties of its derivatives. Its taste is, however, sweet instead of bitter (compare Fischer and Warburg, Abstr., 1906, i, 72; Fischer, Matsubara, and Hilpert, Abstr., 1906, i, 561), and it is lævorotatory, its $[\alpha]_D^{20}$ having the values −14·4° and −36·95° for aqueous and hydrochloric acid solutions respectively.

The naturally occurring dextrorotatory *iso*leucine and all its natural and synthetic derivatives are designated by the prefix *d*- (compare Marckwald, Abstr., 1902, i, 418), whilst the *alloiso*leucine prepared from *d-iso*leucine by a change in the spacial arrangement of the groups round the α-carbon atom is named *d'-alloiso*leucine (compare Fischer, this vol., ii, 148).

d-*Valeraldehyde* (*β-methylbutane-α-al*), $CHMeEt\cdot CHO$, prepared by the oxidation of *d*-amyl alcohol (93%), is a clear, highly refractive liquid, b. p. 90—92°/760 mm., and, assuming the product obtained to contain 93% of the active aldehyde, has $[\alpha]_D^{20}$ +23·56°. If rapidly dried and kept away from the air, the aldehyde remains unchanged for a long time, but it is rapidly oxidised in the air to *d*-valeric acid.

T. H. P.

Resolution of α-Amino-β-methylvaleric Acid into its Optical Isomerides. Properties of the Optically Active Acids and their Derivatives. Identification with Erhlich's *iso*Leucine. René Locquin (*Bull. Soc. chim.*, 1907, [iv], 1, 595—601, 601—607. Compare Erhlich, Abstr., 1903, i, 796; 1904, i, 560; 1906, i, 807; Bouveault and Locquin, 1905, i, 636; 1906, i, 938).—Attempts to resolve *r*-α-amino-β-methylvaleric acid into its optical isomerides by (1) crystallisation of quinine, quinidine, brucine, strychnine, or cinchonine salts of (*a*) its benzoyl derivative or (*b*) of the benzene- or *p*-toluene-sulphonate, or (2) the corresponding camphoramic acid, were unsuccessful.

The resolution was finally effected by crystallisation of the brucine salt of the formyl derivative, the procedure adopted being that described by Fischer and Warburg (Abstr., 1906, i, 72) for leucine.

Ethyl α-formylamino-β-methylvalerate,

$$CHMeEt\cdot CH(CO_2Et)\cdot NH\cdot COH,$$

b. p. 163°/17 mm., D_0^4 1·056, is prepared by heating the ethyl ester of the amino-acid with formic anhydride. It is hydrolysed by water at 165—175°, yielding α-amino-β-methylvaleric acid. The latter, when heated with formic acid at 170° during several hours, furnishes α-formylamino-β-methylvaleric acid, and this on solution in dry alcohol and addition of brucine in the same solvent furnishes a precipitate of the brucine salt (m. p. 150—154°) of the *lævo*-acid still containing a small amount of the *r*-acid, which is readily separated by recrystallisation from warm water. The brucine salt of the *dextro*-acid is obtained by evaporating the mother liquor.

The optically active α-formylamino-β-methylvaleric acids, m. p. 156—157°, separate from water in superb, translucent crystals. The *l*-acid, after being twice recrystallised from water, had $[\alpha]_D^{20}$ $-27·76°$ in alcohol and the *d*-acid $[\alpha]_D^{20}$ $+28·26°$ under the same conditions. A sample of formyl*iso*leucine, prepared by Erhlich, had, according to the latter, m. p. 154—156° and $[\alpha]_D^{20}$ $+25·41$ after a single crystallisation from water.

The optically active α-amino-β-methylvaleric acids crystallise from water in brilliant spangles and have m. p. 280—290°. The *l*-acid has $[\alpha]_D^{20}$ $-10·55°$ in water, $-31·37°$ in dilute hydrochloric acid, and $-40·86°$ in concentrated acid. The *d*-acid has $[\alpha]_D^{20}$ $+11·29°$ in water and $+40·61°$ in concentrated hydrochloric acid.

The lower figures given by Ehrlich for *iso*leucine are probably due to the presence of some *l*-leucine or other impurity in his product.

The *benzoyl* derivative of the *l*-acid, m. p. 118°, crystallises in needles and has $[\alpha]_D^{20}$ $-26·03$ in *N*/2-sodium hydroxide solution (compare Ehrlich, Abstr., 1903, i, 796).

The *benzenesulphonate* of the *r*-acid, m. p. 169°, forms small crystals; that of the *dextro*-acid, m. p. 149°, $[\alpha]_D^{20}$ $-11·63°$ in *N*/3-sodium hydroxide solution, crystallises from benzene. T. A. H.

Metallic Dithiocarbamates; Preparation of Aliphatic Thiocarbimides. MARCEL DELÉPINE (*Compt. rend.*, 1907, **144**, 1125—1127).—In the general method for the preparation of fatty thiocarbimides (Hofmann, *Ber.*, 1868, 1, 25; Ponzio, Abstr., 1896, i, 636) represented by the equations: $CS_2 + 2RNH_2 = R\cdot NH\cdot CS_2\cdot NH_3R$; $2R\cdot NH\cdot CS_2\cdot NH_3R + 2HgCl_2 = 2RNH_3Cl + (R\cdot NH\cdot CS_2)_2Hg + HgCl_2 \longrightarrow 2HgS + 2HCl + 2RN\!:\!CS$, the author prevents the loss of amine as hydrochloride in the first reaction by substitution of a molecule of sodium hydroxide for one molecule of amine, and avoids the formation of hydrochloric acid in the second reaction by using dibasic lead acetate instead of mercuric chloride. Thus the improved method is based on the scheme: $RNH_2 + CS_2 + NaOH = NHR{\cdot}CS_2Na + H_2O$; $NHR{\cdot}CS{\cdot}SNa + OH{\cdot}Pb{\cdot}OAc = RN{:}CS + H_2O + PbS + NaOAc$ (compare Goldschmidt and Schulhof, Abstr., 1886, 557; Losanitsch, Abstr., 1892, 55). The sodium hydroxide can be replaced by potassium or barium hydroxide, and, as the sodium alkyldithiocarbamates are soluble in water, this solvent can be used instead of the alcohol or ether necessary with the anhydrous amines. The method gives good results with methyl-, propyl-, and *iso*butyl-amines, but is not so satisfactory with benzylamine. The solutions of the dithiocarbamates on evaporation give well crystallised salts, which undergo double decomposition with metallic salts. Many of the metallic derivatives formed give the thiocarbimide on boiling with water, and those of iron, nickel, cobalt, and manganese dissolve in ether, chloroform, benzene, and carbon disulphide, giving intensely coloured solutions.

The secondary amines react similarly, giving sodium salts of the constitution $NRR'{\cdot}CS{\cdot}SNa$, which also crystallise well and give metallic salts. The latter are generally soluble in organic solvents, and their solubility in these and insolubility in water increase with the complexity of the alkyl radicles present. The salts of most metals except those of the alkalis and alkaline earths are precipitated by sodium di*iso*butyldithiocarbamate.

The sodium mono- and dialkyl-dithiocarbamates react, as well as the salts of the amines in the reactions previously described, for the formation of the thiuram disulphides and the mono- and dialkyl-dithiocarbamic and iminodithiocarbonic esters. E. H.

Complex Compounds of Organic Imides. IV. The Biuret Reaction. LEO TSCHUGAEFF (*Ber.*, 1907, **40**, 1973—1980. Compare Abstr., 1904, i, 478; 1905, i, 865; 1906, i, 814; Ley and Werner, this vol., i, 302).—Abnormally coloured complex metallic salts of succinimide are obtained when an alkali hydroxide, copper acetate, and excess of the imide interact in aqueous alcoholic solution. They are all of the type $Cu(Su)_4M_2,nH_2O$ or $Cu(Su)_2,2MSu,nH_2O$ [$Su = C_2H_4{:}CO_2{:}N{\cdot}$]. The sodium and lithium salts are coloured blue and ultramarine-blue respectively, the potassium, rubidium, and cæsium salts are all reddish-violet. These compounds are stable in the solid state, but are hydrolysed by water.

Nickel yields a series of similar complex salts of a yellow colour.

Attention is drawn to the similarity in colour and behaviour towards water of the above compounds, and the complex copper derivatives of biurets (Schiff, this vol., i, 206); they differ in composition only in that the biuret compounds contain two molecules of imide, the succinimide derivatives containing four. The conclusion is therefore drawn that the succinimide salts possess the general co-ordinate formula $[Cu(Su)_4]M_2$. W. R.

Cuprammonium Salts. III. DAVID W. HORN (*Amer. Chem. J.*, 1907, **37**, 467—483. Compare Abstr., 1906, ii, 231).—The dependence of the complexity of a cuprammonium compound on the concentration of ammonia, copper salt, and water in the system which it forms is indicated.

The *salt*, $Cu(SCN)_2,2NH_3$, obtained by dissolving cupric thiocyanate in dilute ammonia or by digesting cuprous thiocyanate and dilute ammonia in contact with air, or by treating solutions of potassium or ammonia thiocyanates with dilute ammonia and solutions of cupric salts, forms greyish-blue needles. The salt, $Cu(SCN)_2,4NH_3$, obtained by the addition of potassium or ammonium thiocyanate to a solution of copper sulphate in concentrated ammonia, forms purple-blue crystals, and is identical with the compound already described by Richards and Merigold.

The solubility of copper thiocyanate in ammonia at 25° and 40° respectively was determined, and the results interpreted by aid of the phase rule. A. McK.

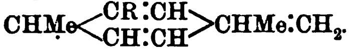
Some Ferrocyanides of Calcium, Barium, and Magnesium. FRANK B. DAINS (*J. Amer. Chem. Soc.*, 1907, **29**, 727—729).—When potassium ferrocyanide is added to a solution of a calcium salt in presence of a large excess of ammonia, a precipitate is produced which is usually regarded as potassium calcium ferrocyanide. An investigation of this precipitate and of similar barium, magnesium, and cadmium salts has shown that these salts contain ammonium and have respectively the composition: $K_2CaFe(CN)_6,4(NH_4)_2CaFe(CN)_6,2H_2O$; $K_2BaFe(CN)_6,4(NH_4)_2BaFe(CN)_6,15H_2O$; $K_2MgFe(CN)_6,5(NH_4)_2MgFe(CN)_6,10H_2O$, and $K_2CdFe(CN)_6,4(NH_4)_2CdFe(CN)_6,2H_2O$. E. G.

The Benzene Problem. IWAN VON OSTROMISSLENSKY (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1351—1387).—A critical survey of the theories which have so far been advanced as to the structure of the benzene nucleus leads to the conclusion that the one which is most probably correct is that of Kekulé, its only weak point being the absence of isomerides in some of the substituted derivatives, as, for instance, in the ortho-compounds. Contrary to Ladenburg's view (*Ber.*, 1869, **2**, 140), it is considered that the impossibility of obtaining such substances is not entirely beyond dispute. With a view to elucidating this question and also of testing Knoevenagel's theory of motor-isomerism (Abstr., 1903, i, 785), a partially successful attempt has been made to obtain the *α*- and *β*-modifications of compounds such as *o*-nitrotoluene, *o*-bromotoluene, *o*-chlorophenol, &c., as well as some of the trisubstituted derivatives. By treating 1-chloro-2 : 4-dinitrobenzene with ammonia, a new 2 : 4-*dinitrophenol* has been obtained, m. p. 85·1°, and differing from the ordinary *o*-dinitrophenol in many of its properties. Reasons are advanced for assuming that these two modifications are not tautomeric forms, but are really due to the different positions of the double linkings in the ring. An attempt is also made to apply crystallographic methods to the solution of the benzene problem, and also, although unsuccessfully, to separate the different modifications by methods analogous to those used by Pasteur. From this point of view the centric formula seems to be altogether untenable; on the other hand, the experimental data are not yet sufficient to lead the author to any quite definite conclusion. Z. K.

Separation of Aromatic Hydrocarbons by the Fractional Precipitation of their Alcoholic Solution. K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1388—1392. Compare Abstr., 1905, i, 405).—In order that the separation of hydrocarbons by means of fractional precipitation should receive a wide application, it is essential that the choice of solvent and precipitant should not be a mere matter of chance, but should depend on certain definite constants which at once indicate their applicability.

The necessary constants are: (1) the solubility of the substances in solvent and in precipitant separately; (2) the solubility of each substance in a mixture of equal volumes of solvent and precipitant. The precipitation will be the more complete the greater the value of $m/2p$, and the less $m'/2p'$ (where m and m' = the solubilities of the substances in the solvent, p = the solubility of one of them in the mixture); p/n (where n = the solubility of one substance in the precipitant) is termed the "characteristic coefficient." The solvent and precipitant must mix with one another. The method has been applied successfully to the separation of a mixture of benzene and toluene, alcohol and water being used as solvent and precipitant. Z. K.

Menthatriene: Determination of Constitution by Optical Methods. AUGUST KLAGES (*Ber.*, 1907, **40**, 2360—2373. Compare Klages and Sommer, Abstr., 1906, i, 566; Rupe and Liechtenhahn, *ibid.*, 374; Brühl, Trans., 1907, **91**, 115).—The constitution of the 2-alkylmenthatrienes is discussed and it is considered that the optical properties exclude the possibility of formulæ containing a trimethylene or a pentamethylene ring. On the other hand, the molecular dispersions, $M_\gamma - M_\alpha$, found exceed those calculated by the same amount, 0·25—0·26, as is the case with the corresponding *p*-cymenes, in which the conjugated ethylene linkings are inactive, whereas the molecular dispersions of similarly constituted compounds containing active conjugated ethylene linkings exceed the calculated dispersions by larger amounts: 0·44 for $\Delta^{1:3}$-dihydro-*m*-xylene, 0·67 for $\Delta^{1:3}$-dihydro-3-ethyl-1 : 5-xylene. Hence the menthatrienes cannot contain conjugated ethylene linkings, and, since their optical properties require a hydrogen atom in position 4, they must have the constitution



$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CR{:}CH}\\\mathrm{CH{:}CH}\end{matrix}{>}\mathrm{CHMe{:}CH_2}$.

2-Phenylmenthatriene cannot be obtained in a state of purity as it readily undergoes transformation into 2-phenyl-*p*-cymene; three specimens, boiling at the same temperature, had α_D + 66°, + 100°, and + 88° respectively. The product obtained on reduction of the specimen, α_D + 88°, with sodium and alcohol, yielded a small amount of an *oil*, b. p. 261°/752 mm., with a changed rotatory power and odour; it could not be separated completely from the 2-phenyl-*p*-cymene constituting the remainder of the product. In yielding a reduction product with sodium and alcohol, 2-phenylmenthatriene resembles phenyl-Δ^1-*cyclo*hexene which contains the grouping CPh:CH and differs from the 2-alkylmenthatrienes and also from such substances as 2-phenyl- and 3-phenyl-1-methyl-Δ^1-*cyclo*hexenes, which contain an ethylene linking, but not the above grouping. These *cyclo*hexenes can be reduced by hydriodic acid, the products having molecular refractions and dispersions similar to those of the normal benzene hydrocarbons, the molecular dispersion found exceeding the calculated by 0·253 for phenyl*cyclo*hexane and by 0·241 for benzyl*cyclo*hexane. This exaltation of the molecular dispersion for 2-phenylmenthatriene, +0·98 for a specimen having a_D +110·2°, is greater than for phenyl*cyclo*hexenes containing the grouping CPh:C : 0·622 for phenyl-Δ^1-*cyclo*hexene, 0·697 for 2-phenyl-1-methyl-Δ^1-*cyclo*hexene, but less than for phenyl*cyclo*hexadiene containing active conjugated ethylene linkings: 1·911 for 3-phenyl-1-methyl-$\Delta^{1:3}$-*cyclo*hexadiene, 1·744 for 3-phenyl-$\Delta^{1:3}$-dihydro-1:5-xylene. The exaltation of the molecular dispersion is normal for hydrocarbons containing one ethylene linking and a phenyl group attached to a saturated carbon atom: 0·227 for benzyl-Δ^1-*cyclo*hexene, 0·300 for 3-benzyl-1-methyl-Δ^1-*cyclo*hexene.

As a derivative of diphenyl, 2-phenyl-*p*-cymene has an exaltation of the molecular dispersion, 0·79, greater than that for 2-benzyl-*p*-cymene, 0·49.

Refractive indices are given for the sodium *D*-line, and for α-, β-, and γ-hydrogen lines; those for the *D*-line only are quoted here.

2-Methylmenthatriene, D_4^{15} 0·8776, $[a]_D^{21}$ +69·12°, n_D^{15} 1·50217, $M_\gamma - M_a = 1{\cdot}94$. 2-Methyl-*p*-cymene, $D_4^{15\cdot5}$ 0·8740, $n_D^{15\cdot5}$ 1·50001, $M_\gamma - M_a = 1{\cdot}94$.

2-Ethyl-*p*-cymene, formed by Fittig's reaction from 2-iodo-*p*-cymene, b. p. 100°/17 mm., $D_4^{15\cdot7}$ 0·8706, n_D^{15} 1·49670, $M_\gamma - M_a = 2{\cdot}07$; the corresponding ***sulphonanilide***, m. p. 150—151°. 2-Ethyl-*p*-cymene, from 2-ethylmenthatriene, $D_4^{15\cdot6}$ 0·8708, $n_D^{15\cdot6}$ 1·49878, $M_\gamma - M_a = 2{\cdot}07$. 2-Ethylmenthatriene, D_4^{15} 0·8880, n_D^{15} 1·50847, $M_\gamma - M_a = 2{\cdot}07$.

2-*Propyl*-$\Delta^{6:8(9)}$-*menthadiene-2-ol* (*2-propylcarveol*), $C_{13}H_{22}O$, prepared by the action of magnesium propyl bromide on carvone, is a colourless, viscid oil with a feeble odour, b. p. 125°/15 mm., D_4^{21} 0·9178, $[a]_D^{21}$ +49·16°, n_D^{21} 1·4885.

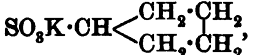
2-***Propylmenthatriene***, $C_{13}H_{20}$, prepared by treating the product of the action of magnesium propyl bromide on carvone with an ice-cold mixture of glacial acetic acid and acetic anhydride, is obtained as a mobile oil, b. p. 107—108°/13 mm., D_4^{15} 0·8804, $[a]_D^{22}$ +86·20°, n_D^{15} 1·50273, $M_\gamma - M_a = 2{\cdot}22$, and decolorises bromine instantaneously.

2-***Propyl-p-cymene***, $C_{13}H_{20}$, formed in a 60% yield by heating 2-propylmenthatriene with 3% hydrochloric acid, b. p. 226°/766 mm. (corr.) or 106—107·5°/13 mm., D_4^{15} 0·8685, n_D^{15} 1·49585, $M_\gamma - M_a = 2{\cdot}21$. The ***sulphonic acid*** crystallises in colourless needles, m. p. 69—71°; the ***sulphonyl chloride*** crystallises in rhombic plates, m. p. 61°; the ***sulphonanilide***, $C_{19}H_{25}O_2NS$, forms strongly refracting plates, m. p. 138°. 2-Propyl-*p*-cymene is converted by the action of bromine and aluminium bromide into pentabromotoluene, m. p. 283°.

2-Phenylmenthatriene, D_4^{15} 0·9752, $[a]_D^{13\cdot8}$ +110·2°, n_D^{15} 1·56914, $M_\gamma - M_a = 3{\cdot}63$. 2-Phenyl-*p*-cymene, b. p. 143°/14 mm., D_4^{15} 0·9776, n_D^{15} 1·56797, $M_\gamma - M_a = 3{\cdot}44$; the ***sulphonic acid*** forms glistening crystals containing water of crystallisation, m. p. 109—115°; the *sulphonyl chloride* forms small leaflets, m. p. 173°; the *sulphonanilide*, $C_{22}H_{23}O_2NS$, crystallises in plates, m. p. 209°. The action of bromine and aluminium bromide on 2-phenyl-*p*-cymene leads to the formation of *octabromo-o-methyldiphenyl*, $C_{13}H_4Br_8$, which crystallises in yellow needles, m. p. 345—350°.

2-*Benzyl*-p-*cymene*, $C_{17}H_{20}$, b. p. 176—177°/17 mm. or 296—297°/743 mm., D_4^{15} 0·9690, n_D^{15} 1·55650, $M_\gamma - M_\alpha = 3·25$, is formed from 2-*benzylidenementhadiene*, $[\alpha]_D^{21}$ + 177·35°. 2-*Benzyl*-p-*cymenedisulphonic acid* crystallises in leaflets, m. p. 71—72°; the *disulphonyl chloride*, m. p. 134°, crystallises from light petroleum; the *disulphonanilide*, $C_{23}H_{25}O_2NS$, forms colourless crystals, m. p. 88—103°. *Nonabromo-o-methyldiphenylmethane*, $C_{14}H_5Br_9$, formed by the action of bromine and aluminium bromide on 2-benzyl-*p*-cymene, crystallises in yellow needles, m. p. 281°. G. Y.

Alicyclic Compounds containing Sulphur. WALTHER BORSCHE and W. LANGE (*Ber.*, 1907, **40**, 2220—2225. Compare Abstr., 1905, i, 765; 1906, i, 165).—*Potassium* cyclo*pentanesulphonate*,

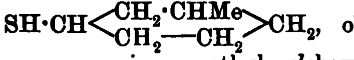


$$SO_3K\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix},$$

obtained by forming the sulphinic acid by the action of sulphur dioxide on magnesium *cyclo*pentyl bromide and then oxidising it with permanganate, crystallises in leaflets. It was converted into the sulphonyl chloride from which the acid was obtained as colourless, hygroscopic crystals, which, in ethereal solution, combine with aniline to form cyclo*pentanesulphonanilide*, $C_5H_9\cdot SO_2\cdot NHPh$, separating from dilute alcohol in needles, m. p. 89·5—90·5°.

For the preparation of 1-methyl*cyclo*hexane-3-sulphonic acid, methyl*cyclo*hexane-3-ol was converted into 3-chloromethyl*cyclo*hexane by heating with fuming hydrochloric acid for five hours at 100°. By the action of sulphur dioxide on the Grignard reagent, prepared from the latter compound, a sulphinic acid was obtained, which was oxidised by permanganate to form *potassium methyl*cyclo*hexane*-3-*sulphonate*, $C_7H_{13}O_3SK$, which separates from water in leaflets and from absolute alcohol in silvery scales. The corresponding *sulphonyl chloride* has b. p. 143—144°/14 mm. (decomp.), and, when warmed with water, gives the *acid*, $C_7H_{14}O_3S,2H_2O$, which separates from dilute alcohol in hygroscopic needles, m. p. 93—94°.

As by-products from the Grignard reaction mentioned, the following were obtained: unchanged methylhexanol, 3:3′-dimethyldi*cyclo*hexyl, m. p. 263—264°, and 3:3′-dimethyldi*cyclo*hexyl sulphoxide. The latter was converted by oxidation into the corresponding sulphone.

*Methyl*cyclo*hexyl 3-hydrosulphide*,  $SH\cdot CH<\begin{matrix}CH_2\cdot CHMe\\ CH_2\text{—}CH_2\end{matrix}>CH_2$, obtained by the action of sulphur on magnesium methyl*cyclo*hexyl chloride, is a colourless liquid, b. p. 172—174°. A. McK.

Some Derivatives of Phenyl*cyclo*hexane. NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1295—1303. Compare Abstr., 1902, i, 20).—Phenyl*cyclo*hexane when heated with nitric acid, D 1·075, in sealed tubes yields chiefly 1-*nitrophenyl*cyclo*hexane*,

$CH_2<\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}>CPh\cdot NO_2$, m. p. 54·5—56°, which crystallises in long needles, also a mixture of other *nitro*-derivatives, $C_6H_{10}Ph\cdot NO_2$, m. p. 86—89°, and small quantities of hydrocyanic, benzoic, glutaric, and succinic acids.

The corresponding 1-*amine*, b. p. 180·5—182·5°/66 mm., is obtained by heating the nitro-derivative with tin and hydrochloric acid; it is insoluble in water, and absorbs carbon dioxide from the air, forming a solid *carbonate*. The following salts are described: *hydrochloride*, m. p. 230—230·5°; *nitrate*, m. p. 173° (decomp.); *sulphate*, m. p. 226—227·5°; *nitrite*, decomposing at 70—80°; *acetate*, m. p. 154—155·5°; and *platinichloride*, $(C_{12}H_{15}NH_2)_2,H_2PtCl_6$, m. p. 177°. The *compound* $NHPh\cdot CN\cdot NH\cdot C_6H_{10}Ph$, m. p. 156°, is also described. 1-*Phenyl*cyclo*hexane*-1-*ol*, $CH_2<\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}>CPh\cdot OH$, obtained by heating 1-amino-1-phenyl*cyclo*hexane with nitrous acid, forms monoclinic crystals [$a:b:c = 1\cdot9033:1:1\cdot8227$; $\beta = 79°19'$], m. p. 62—63·5°, b. p. 151°/20 mm. Z. K.

The Hydrocarbon $C_{13}H_{18}$. NICOLAI KURSANOFF (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 1304—1316. Compare preceding abstract).—Friedel and Craft's reaction is equally applicable to the chlorine compounds of the *cyclo*hexanes as it is to those of the aliphatic derivatives, and the phenyl*cyclo*hexanes so produced have all the properties of aromatic compounds with a fatty side-chain. The chloro*cyclo*hexane, when treated with toluene and aluminium chloride, yields a mixture of isomeric *tolyl*cyclo*hexanes*, which could not be separated by fractional distillation. The mixture was therefore treated with sulphuric acid, then neutralised with sodium hydroxide; of the mixture of *sodium sulphonates* thus obtained, one,

$$C_6H_{11}\cdot C_6H_3Me\cdot SO_3Na,$$

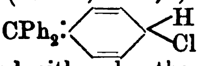
could be isolated by reason of its complete insolubility in benzene. When treated with concentrated hydrochloric acid, it yields m-*tolyl*cyclo*hexane*, b. p. 257—257·3°/754 mm., n_D^{18} 1·5236, D_4^{18} 0·9365. This, when oxidised with dilute nitric acid, yields *iso*phthalic acid. The soluble sodium sulphonates when treated with phosphorus pentachloride yield a mixture of the *compounds* $R\cdot SO_2Cl$; neither these nor the corresponding *amides*, $RSO_2\cdot NH_2$, could be crystallised, but the chlorides on treatment with aniline yield a mixture of *anilides*, one of which is a crystalline substance insoluble in petroleum, $C_6H_{11}\cdot C_6H_3Me\cdot SO_2\cdot NHPh$, m. p. 186·5—187·5°. When treated with hydrochloric acid, it forms p-*tolyl*cyclo*hexane*, $CMe<\substack{CH\cdot CH\\ CH\cdot CH}>C\cdot C_6H_{11}$, b. p. 259·8—260°/750 mm., n_D^{18} 1·5232, D_4^{18} 0·9365, which with nitric acid yields terephthalic acid. Its odour and properties are similar to the meta-derivative. The other anilides when heated in sealed tubes with fuming hydrochloric acid yielded a mixture of complex hydrocarbons. 3-*Phenyl*-1-*methyl*cyclo*hexane*, $CHMe<\substack{CH_2\cdot CHPh\\ CH_2—CH_2}>CH_2$, obtained by the action of benzene on chloromethyl*cyclo*hexane in the presence of aluminium chloride, is a liquid with an odour resembling that of lemon, b. p. 249°/730 mm., D_4^{18} 0·9425, n_D^{18} 1·5246; its properties are similar to those of the other isomerides of the hydrocarbon $C_{18}H_{18}$. Z. K.

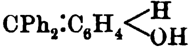
Triphenylmethyl. II. JULIUS SCHMIDLIN (*Ber.*, 1907, **40**, 2316—2329. Compare Abstr., 1906, i, 392; this vol., i, 26).—*p*-Benzoyltriphenylmethane has been obtained from *p*-tolylphenyl ketone by conversion into the ω-dibromo-derivative (Bourcet, Abstr., 1897, i, 566) and condensing this with benzene and aluminium chloride. The product melts at 165·5—166° (corr.) and is identical with the substance obtained by the action of benzaldehyde on the α-form of magnesium triphenylmethyl chloride. When a fresh benzene solution of the α-magnesium compound is decomposed by dilute hydrochloric acid, no trace of hydrogen is evolved.

The reaction between triphenylmethyl chloride and magnesium in dry ether, if necessary, with the addition of benzene, and in the presence of a little iodine, has been investigated. The liquid after boiling for some time was decomposed with dilute sulphuric acid and the amounts of magnesium sulphate and triphenylmethyl (as peroxide) determined. In many experiments the amount of magnesium sulphate was less than that corresponding with the triphenylmethyl, assuming the latter to be formed according to the equation $CPh_3{\cdot}MgCl + HCl = MgCl_2 + CPh_3 + H$. When, however, the heating is continued for fifty to one hundred minutes, the amount of sulphate is in excess of the triphenylmethyl. An explanation of these phenomena is offered.

Both α- and β-compounds yield triphenylmethyl when treated with triphenylmethyl chloride, but in order to obtain a good yield it is essential that the ether used in the preparation of the magnesium compound should be absolutely dry. The dryness of the ether is indicated by the formation of a voluminous precipitate when the ethereal solution of triphenylmethyl chloride has been heated with magnesium and a little iodine for an hour. Although the α- and β-compounds yield different products with benzaldehyde and the same derivative with triphenylmethyl chloride, experiments have shown that it is the same β-derivative which yields β-benzopinacoline with benzaldehyde, and triphenylmethyl with triphenylmethyl chloride. Similar experiments with the α-compound did not give conclusive evidence. J. J. S.

Tautomerism in the Triphenylmethane Series. FRIEDRICH KEHRMANN and FRANZ WENTZEL (*Ber.*, 1907, **40**, 2755—2756. Compare Gomberg, this vol., i, 504).—The authors claim that Gomberg's interpretation of the nature and cause of the basic character of the tautomeric carbinol salts is not essentially different from their theory (Abstr., 1901, i, 638).

They compare  with ammonium chloride and regard it as derived either by the addition of hydrogen chloride to the radicle $CPh_2{:}C_6H_4{<}$ or by substitution from the base



$$CPh_2{:}C_6H_4{<}^{H}_{OH}$$

E. F. A.

Terpenes and Ethereal Oils. LXXXV. Behaviour of the Nitrites of Primary Bases and Enlargement of Rings in Carbocyclic Systems. OTTO WALLACH (*Annalen*, 1907, **353**, 318—334).—It is found that the nitrites of primary aliphatic bases can be prepared by the action of commercial, alkaline sodium nitrite on the concentrated aqueous solution of the hydrochloride, that is, in the complete absence of free acid. The resulting nitrite may be isolated if less soluble than the hydrochloride, and is then sufficiently stable to permit of recrystallisation from boiling water, but is decomposed on addition of traces of a free acid. The nitrites of primary alicyclic amines are even more stable (Wallach and Griepenkerl, Abstr., 1892, 1238). l-*Menthylamine nitrite* crystallises in needles, decomposes at about 139°, and yields menthol when boiled with water containing a drop of acetic acid. *Pinylamine nitrite* forms stout crystals, decomposes at about 125°, and when treated with acids yields chiefly pinocarveol.

Stable, sparingly soluble nitrites of secondary bases have been described previously (*loc. cit.*; Abstr., 1906, i, 514).

Primary aromatic amines, which form sparingly soluble nitrates, yield also sparingly soluble nitrites. m-4-*Xylidine nitrite* is formed in white crystals, which when dried become yellow and decompose to a reddish-brown oil; the crystals yield *m*-4-xylidine with aqueous alkalis, phenol when boiled with dilute acetic acid, or a solution of the diazosulphate when treated with sulphuric acid.

The decomposition of nitrites of primary alicyclic amines in boiling aqueous solution on addition of a free acid, takes place mainly in two directions: (1) the formation of a hydrocarbon, and (2) the formation of an alcohol, or of two or more isomeric alcohols. Thus, whilst *l*-menthylamine nitrite gives *l*-menthol, *d*-menthylamine nitrite yields chiefly menthene. *iso*Thujylamine nitrite is converted almost completely into a hydrocarbon, whilst under the same conditions thujylamine nitrite yields much alcohol. It is found now that when boiled with water and acetic acid, the nitrites of cyclylmethylamines (compare this vol., i, 616) yield small amounts of hydrocarbons and of the alcohols corresponding to the amines, together with the alcohols of the next higher ring system (compare Demjanoff, Abstr., 1904, i, 410). As the cyclylmethylamines are prepared from *cyclo*ketones and *cyclo*ketones are formed by oxidation of the alcohols produced by the decomposition of the nitrites, the whole series of reactions constitutes a method of enlarging carbocyclic systems. In this manner, *cyclo*hexanone is formed from *cyclo*pentanone, *cyclo*heptanone (suberone) from *cyclo*hexanone, and azaleone (*cyclo*octanone) from suberone.

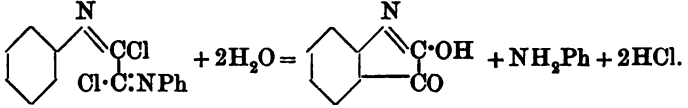
Azaleone (Mager, Abstr., 1893, i, 558; Derlon, Abstr., 1898, i, 638; Miller and Tschitschkin, Abstr., 1899, i, 789) crystallises when cooled, m. p. 25—26°, b. p. 195—197°, D^{20} 0·9581, n_D 1·4694; the semicarbazone, m. p. 163—164·5°. The ketone yields suberic acid on oxidation with chromic and sulphuric acids.

The following constants are given for the pure ketones and their derivatives: *cyclo*pentanone, b. p. 129°, D^{20} 0·948, n_D 1·4366; semicarbazone, 206°; dibenzylidene derivative, m. p. 189°. *cyclo*Hexanone,

b. p. 155°, D^{21} 0·947, n_D 1·4503; semicarbazone, m. p. 165—166°; dibenzylidene derivative, m. p. 117—178°. *cyclo*Heptanone, b. p. 180°, D^{21} 0·9500, n_D 1·4604; semicarbazone, m. p. 163°; dibenzylidene derivative, m. p. 108°. G. Y.

Imino-chlorides of Oxalic Acid. RUDOLPH BAUER (*Ber.*, 1907, 40, 2650—2662).—Imino-chlorides of the type R·N:CCl·CCl:NR have been prepared by Wallach and Bischoff by the action of phosphorus pentachloride on the substituted oxamides. A much better method is to heat the materials in a solvent such as benzene or toluene. The imino-chlorides prepared are well characterised substances, and, although similar in properties to those obtained from monobasic acids, are more stable. Diphenyloxalimino-chloride, NPh:CCl·CCl:NPh, is obtained in 70% yield when toluene is used as solvent; with benzene no imino-chloride was isolated. It crystallises in straw-yellow needles, m. p. 115°, and is stable in dry air; moisture, however, slowly converts it into oxanilide (compare Wallach, Abstr., 1881, 718). A 90% yield of di-*o*-tolyloxalimino-chloride (oxalotoluidiminochloride) is obtained when benzene is used as solvent (Bischoff, Abstr., 1894, i, 514). The *di*-p-*tolyl*- and *di*-m-*tolylimino-chlorides* have m. p. 107° and 72° and are yellow.

These imino-chlorides, when added to pure concentrated sulphuric acid at the temperature of the water-bath, yield isatin or methylisatins; no intermediate product has as yet been isolated. This reaction has no analogy, and may be represented by:



The yield of isatin is 15%, of *o*- and *p*-methylisatins, 49% and 19%, whilst it is very small in the case of the meta-compound. 7-*Methylisatin*, $C_9H_7O_2N$, crystallises in red, hair-like needles, m. p. 266°; the *phenylhydrazone*, $C_{15}H_{13}ON_3$, forms golden-yellow needles, m. p. 242°, and the *oxime*, $C_9H_8O_2N_2$, yellow needles, m. p. 235°. 4-*Methylisatin* forms red leaflets, m. p. 155°. The *methylisatin*, obtained from the di-*m*-tolyloxalimino-chloride, has m. p. 165°, and may be identical with Findeklee's 6-methylisatin, m. p. 169° (Abstr., 1906, i, 43).

The imino-chlorides react with bases like acid chlorides; with alcoholic ammonia, diphenyloxalimino-chloride gives diphenyloxalamidine; aniline yields *tetraphenyloxalamidine*, NPh:C(NHPh)·C(NHPh):NPh, m. p. 153°, and crystallising in light yellow prisms; its *picrate* has m. p. 182°. With phenylhydrazine, *tetraphenyloxalhydrazidine*, NPh:C(NH·NHPh)·C(NH·NHPh):NPh, is obtained in yellow needles, m. p. 200°; ferric chloride oxidises it to a dark red osotetrazone.

Diphenyloxalimino-chloride is decomposed by alcoholic potassium hydroxide; with the di-*o*-tolyl derivative, however, a mixture is obtained, the less soluble constituent of which is *diethyl di*-o-*tolyliminooxalate*, C_7H_7·N:C(OEt)·C(OEt):N·C_7H_7, m. p. 92°; the more soluble is *ethyl* o-*tolylimino*-o-*tolyloxamate*, C_7H_7·NH·CO·C(OEt):N·C_7H_7, m. p. 91°.

Tetra-o-*tolyloxalamidine*, $C_{30}H_{30}N_4$, forms light yellow plates from a mixture of light petroleum and benzene; m. p. 169°. W. R.

Platinum Compounds of Phenylcarbylamine and of Benzonitrile. LUDWIG RAMBERG (*Ber.*, 1907, 40, 2578—2588. Compare Hofmann and Bugge, this vol., i, 489).—The *substance* $[Pt(CNPh)_2Cl_2]_x$, obtained by adding slowly an aqueous suspension of phenylcarbylamine to a solution of an excess of potassium platinosochloride, is a violet-blue, amorphous powder which does not dissolve unchanged in the usual solvents. By heating at 110—115° or by prolonged boiling with chloroform or acetone, it changes into the colourless *chloride*, $Pt(CNPh)_2Cl_2$, m. p. 257—258°; this forms well-defined, monoclinic crystals [$a : b : c = 1·1113 : 1 : 0·8391$; $\beta = 101°53'$], and by treatment with concentrated sulphuric acid at 110—115° yields colourless needles of a *substance* of unknown composition, which is reconverted into the chloride, $Pt(CNPh)_2Cl_2$, by treatment with potassium chloride, and forms the iodide, $Pt(CNPh)_2I_2$, by the action of potassium iodide, a mixture of the bromide and chloride by the action of potassium bromide, and a mixture of the chloride and of the thiocyanate by the action of potassium thiocyanate.

The brownish-violet *compound*, $[Pt(CNPh)_2Br_2]_x$, is obtained in a similar manner to the corresponding chloride, and, like the latter, changes into colourless *dibromobisphenylcarbylamineplatinum*, $Pt(CNPh)_2Br_2$, m. p. 245°, which forms monoclinic crystals [$a : b : c = 1·1303 : 1 : 0·8496$; $\beta = 103°9'$], and is not attacked by concentrated sulphuric acid in the cold.

Di-iodobisphenylcarbylamineplatinum, $Pt(CNPh)_2I_2$, m. p. 241°, prepared as mentioned above, separates from chloroform in yellow, monoclinic crystals [$a : b : c = 0·554 : 1 : 0·369$; $\beta = 99°19'$], and occasionally in slender needles, which change rapidly into the stable form; by the addition of iodine to a warm solution of the iodide in chloroform, black needles of a *hexaiodide*, $Pt(CNPh)_2I_6$, are obtained.

Dinitritobisphenylcarbylamineplatinum, $Pt(CNPh)_2(NO_2)_2$, is prepared from phenylcarbylamine and potassium platinonitrite in aqueous solution; it separates from acetone in slender, yellow needles, which lose acetone and become dark red; the red crystals turn yellow at 100—110° and decompose at 155—160° without melting.

Dichlorobisbenzonitrileplatinum, $Pt(NCPh)_2Cl_2$, prepared by the prolonged heating of benzonitrile and a solution of potassium platinochloride at 60—70°, separates from acetone in small, yellow prisms or leaflets, has m. p. 219—220° (decomp.), and is deposited from chloroform or benzene solution in crystals containing 2 mols. of the solvent. The substance is easily soluble in hot benzonitrile, and on cooling, small, yellow needles separate which have the same composition and m. p. as the original chloride, but are more soluble in acetone; this solvent changes them partially into the original substance. Concentrated sulphuric acid dissolves the chloride with effervescence; the clear solution yields with potassium chloride the original chloride, and with potassium iodide the corresponding iodide mixed with the chloride. A yellow, crystalline *substance*, $Pt(NCPh)_2Cl_4$, m. p. 114—115° (decomp.), is precipitated when chlorine is passed into a solution of the chloride in chloroform.

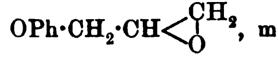
Dibromobisbenzonitrileplatinum, $Pt(NCPh)_2Br_2$, m. p. 218—220°, is obtained by the prolonged heating of benzonitrile (2 mols.), a solution of potassium platinosochloride (1 mol.), and potassium bromide (>4 mols.) at 60—70°. The substance separates from acetone in orange-yellow plates or prisms, and from chloroform with $2CHCl_3$; like the chloride it exists in two isomeric forms and yields a red, crystalline additive *compound*, $Pt(NCPh)_2Br_4$.

The nature of the isomerism of these platinum derivatives is not yet elucidated. C. S.

Two New Methods for the Preparation of *cyclo*Butanol. Nikolaus J. Demjanoff and M. Dojarenko (*Ber.*, 1907, **40**, 2594—2597).—Silver *cyclo*butanecarboxylate, iodine, and powdered glass are heated on the water-bath and the product distilled under 40—60 mm. pressure. The distillate contains *cyclo*butanecarboxylic acid and its *ester* with *cyclo*butanol. The latter, $C_4H_7\cdot CO_2\cdot C_4H_7$, b. p. 198·5—199°/750 mm., is a colourless, mobile liquid, which has D_{15}^{15} 1·0033 and n_D^{19} 1·4551; by hydrolysis with 25% potassium hydroxide at 110—120°, the ester yields *cyclo*butanol, b. p. 123°/733 mm., D_{15}^{15} 0·9226, and n_D^{19} 1·4339, which yields succinic acid by oxidation with nitric acid.

The same alcohol and ester are obtained by the electrolysis of a solution containing potassium *cyclo*butanecarboxylate, potassium carbonate, and potassium hydrogen carbonate.

*cyclo*Butanol and phenylcarbimide react to form a *phenylurethane*, $C_4H_7O\cdot CO\cdot NHPh$, m. p. 110—111°, which separates from dilute alcohol in glistening prisms. C. S.

Condensation of Epichlorohydrin with Phenols. Paul Cohn and Robert Plohn (*Ber.*, 1907, **40**, 2597—2602. Compare Cohn and Friedländer, Abstr., 1904, i, 866; Lindemann, Abstr., 1891, 1198).—*Phenyl glycide ether*,  $OPh\cdot CH_2\cdot CH{<}\begin{matrix}CH_2\\ |\\ O\end{matrix}$, m. p. 82°, is obtained by heating together a solution of sodium phenoxide and epichlorohydrin, by adding concentrated sodium hydroxide to equal molecular quantities of epichlorohydrin and phenol, or by heating the same two substances with alcoholic sodium ethoxide. 2 : 4 : 6-*Tribromophenyl glycide ether* has m. p. 85°, and p-*tolyl glycide ether*, 88°.

Dichlorohydrin and potassium phenoxide yield phenyl glycide ether, and Rössing's so-called acetyldiphenylglyceryl ether (Abstr., 1886, 345) is also the same substance. C. S.

Derivatives of Quinol Dimethyl Ether. Hugo Kauffmann and Karl Burr (*Ber.*, 1907, **40**, 2352—2358).—The auxochromic effect of the methoxyl group is found to be intensified when two methoxyls are present in the para-position to one another.

β-Cyano-2 : 5-dimethoxystilbene, $C_6H_3(OMe)_2\cdot CH\!:\!CPh\cdot CN$, formed by condensation of 2 : 5-dimethoxybenzaldehyde with phenylacetonitrile in alcoholic sodium hydroxide solution, crystallises in intensely yellow needles, m. p. 69°, and forms yellow solutions with greenish-blue fluorescence in dissociating, but less intensely-coloured solutions with a more violet fluorescence in other, solvents. The corresponding chromogen, cyanostilbene, is colourless.

2 : 5-*Dimethoxybenzylideneindandione*,

$$C_6H_3(OMe)_2\cdot CH\colon C<\overset{CO}{\underset{CO}{}}>C_6H_4,$$

prepared by heating 1 : 3-diketohydrindene with 2 : 5-dimethoxybenzaldehyde in alcoholic solution, crystallises in orange-red needles, m. p. 149°, and forms yellow to yellowish-red solutions with greenish-yellow fluorescence. The chromogen, benzylideneindandione, is light yellow.

2 : 5-Dimethoxycinnamic acid forms yellowish-green crystals, m. p. 147° (143°: Schnell, Abstr., 1884, 1164), and gives a brownish-yellow colour with concentrated sulphuric acid. The chromogen is colourless. *Ethyl* 2 : 5-*dimethoxycinnamate*, $C_{13}H_{16}O_4$, is obtained as a strongly refracting, yellowish-green liquid with blue fluorescence, b. p. 216°/20 mm., D^{26}_{26} 1·1357; has a brilliant fluorescence in very dilute solutions, and forms a yellow solution in concentrated sulphuric acid. The liquid chromogen is colourless.

2 : 5-*Dimethoxybenzylidenemalonic acid*, $C_6H_3(OMe)_2\cdot CH\colon C(CO_2H)_2$, prepared by heating 2 : 5-dimethoxybenzaldehyde with malonic acid in glacial acetic acid solution on the water-bath, crystallises in yellow prisms with greenish-yellow fluorescence, m. p. 188° (decomp.), and forms in alcohol a yellow solution with blue fluorescence which becomes colourless, but with violet fluorescence, on addition of an alkali. The chromogen, benzylidenemalonic acid, is colourless.

2 : 5-*Dimethoxybenzylidenesemicarbazone*,

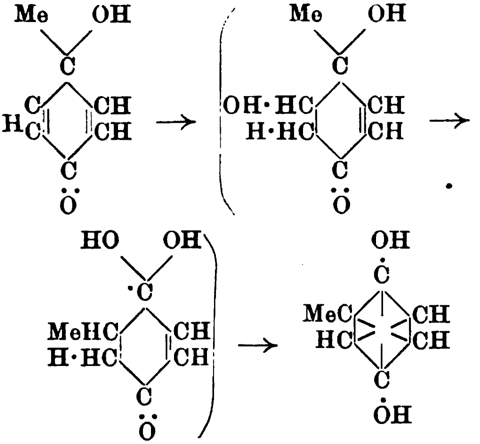
$$C_6H_3(OMe)_2\cdot CH\colon N\cdot NH\cdot CO\cdot NH_2,$$

crystallises in white needles, m. p. 208°, and dissolves in glacial acetic acid or hot alcohol, forming solutions with violet fluorescence. This is believed to be the first semicarbazone the fluorescence of which can be observed directly.

2 : 2′ : 5 : 5′-*Tetramethoxybenzylideneazine*, $N_2[CH\cdot C_6H_3(OMe)_2]_2$, crystallises in yellow needles, m. p. 160°, detonates when highly heated, and forms red *salts* which have a red fluorescence when observed through a blue screen.

2 : 5-*Dimethoxybenzylideneaniline*, $C_6H_3(OMe)_2\cdot CH\colon NPh$, is obtained as a strongly refracting, viscid, yellow oil, b. p. 239°/20 mm., $D^{23\cdot5}_{23\cdot5}$ 1·1422, and dissolves in organic solvents, forming solutions which are not fluorescent; the *salts* are intensely yellow, and show a yellow fluorescence when observed through a blue screen. G. Y.

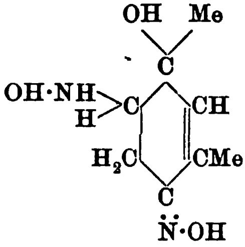
Action of Hydroxylamine on 2 : 4-Dimethylquinol and its Ethers. EUGEN BAMBERGER and L. RUDOLF (*Ber.*, 1907, 40, 2236—2258. Compare this vol., i, 519, 520).—The transformation of quinols into ketonic quinol or resorcinol derivatives is undoubtedly accompanied by the formation of intermediate products. To take one case, the simplest ketonic quinol transformation, namely, the conversion of ketonic compound into toluquinol, is expressed by the following scheme:



To support this hypothesis it was desirable to prove the presence of such additive compounds. The additive compounds of water and alcohol cannot be isolated. In the present communication the property possessed by quinols of uniting with hydroxylamine or phenylhydrazine is, however, shown and the structure of the intermediate products proved.

The action of hydroxylamine on ketonic 2 : 4-dimethylquinol and on its ethyl and methyl ethers has been studied. The action on the quinol itself is represented by the equation: $OH{\cdot}C_8H_9O + 2NH_2{\cdot}OH = H_2O + OH{\cdot}C_8H_{18}N_2O_3$. The hydroxyl group does not play a part in this reaction, since the action of the ketonic quinol ethers is represented by $OR{\cdot}C_8HO_9 + 2NH_2{\cdot}OH = H_2O + OR{\cdot}C_8H_{18}N_2O_3$.

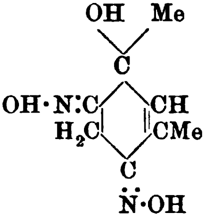
The product of the action of hydroxylamine on ketonic xyloquinol has the property of a hydroxylamino-compound, $R{\cdot}NH{\cdot}OH$, and is represented by the formula (I). It possesses the properties typical of a β-substituted hydroxylamine. It is soluble not only in alkalis, but also in mineral acids, it exhibits reducing properties towards Fehling's solution, &c., and it combines with diazo-salts, benzaldehyde, and acetone respectively. It forms a tribenzoyl derivative insoluble in alkali hydroxides. It is reduced by stannous chloride to a xylylenediamine. The compound in question is accordingly designated as *hydroxylaminohydroxyketodimethyltetrahydrobenzene oxime*; it separates from alcohol in glistening needles and decomposes at about 169°. When its alcoholic solution is boiled with benzaldehyde, glistening leaflets of the *benzylidene* compound, $C_{15}H_{18}O_3N_2$, separate, m. p. 218° (decomp.). The alkaline solution of the latter compound reduces Fehling's solution very slowly in the cold. The o-*nitrobenzylidene* derivatives form colourless, nacreous needles, decomposing at 239°. The m-*nitrobenzylidene* derivative forms glistening, colourless plates, decomposing at 216·5°. The p-*nitrobenzylidene* derivative forms orange-yellow, glassy, quadratic plates, decomposing at 207°. The o-*nitrodiazobenzene* derivative, $OH{\cdot}C_6H_4{\cdot}N_2{\cdot}N(OH){\cdot}C_6H_4Me_2(OH){:}N{\cdot}OH$, forms orange-yellow, glistening, rhombic plates, m. p. 196·5°. The p-*nitrodiazobenzene* derivative separates in yellow, glistening leaflets, m. p.



(I.)

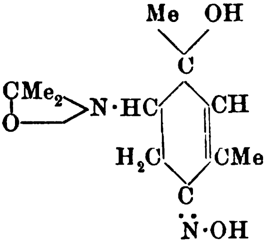
220·5°. The *tribenzoyl* derivative forms glistening needles, m. p. 149—150°.

Since the oxime in question is of the type CHRR'·NH(OH), it readily loses two atoms of hydrogen on oxidation by Caro's acid, being converted into *hydroxydiketodimethyltetrahydrobenzene dioxime*, m. p. 176° (decomp.), when heated quickly. This substance has not basic properties, but is distinctly acidic, and with benzoyl chloride gives, accordingly to the conditions, either a dibenzoyl derivative, soluble in alkali, or a tribenzoyl derivative soluble in alkali. The *dibenzoyl* derivative forms silky needles, m. p. 141° (decomp.), whilst the *tribenzoyl* derivative forms silky needles, m. p. 153° (decomp.).



The oxidation of the hydroxylaminoquinol monoxime may also be effected with ferric chloride. When the monoxime is acted on by nitrous acid, it is converted into a *compound* with the probable formula $C_{16}H_{25}O_7N_5$, which has the properties of a nitrosoamine, forms glistening crystals, and decomposes at about 183·5°. The monoxime was also reduced by stannous chloride to form 1:3-dimethylphenylene-4:6-diamine.

The *condensation product*, obtained from acetone and the hydroxylaminoquinoloxime in the presence of a trace of hydrochloric acid, forms glistening, hexagonal plates, m. p. 195·5° (decomp.). It is at once decomposed by mineral acids to regenerate acetone and the original oxime. Its *dibenzoyl* derivative has m. p. 145—146° and does not dissolve in alkalis. The condensation product in question is readily soluble in alkalis, does not reduce cold Fehling's solution, or condense with phenylhydrazine or with *p*-nitrophenylhydrazine. In the presence of hydrogen ions, it is without action on diazo-salts in neutral solution; however, 2 mols. combine with 1 mol. of diazo-compound with the elimination of 1 mol. H_2O. With *p*-nitrodiazobenzene nitrate, it forms the *compound*, $C_{28}H_{39}O_8N_7$, an amorphous substance, m. p. 150° (decomp.). Its solution in sodium hydroxide is raspberry-coloured, whilst its alcoholic solution gives a green coloration with ferric chloride. With *o*-nitrodiazobenzene nitrate, it forms the *compound*, $C_{28}H_{39}O_8N_7$, which also could not be obtained crystalline; its solution in alkalis is carmine-red, whilst its alcoholic solution gives a dark green coloration with ferric chloride.



The condensation product also combines with benzaldehyde to form the *compound* $C_{15}H_{18}O_3N_2$, which crystallises in glistening leaflets, m. p. 218°.

Hydroxylaminoketoethoxydimethyltetrahydrobenzene oxime, obtained from ketonic 2:4-dimethylquinol ethyl ether, hydroxylamine, and methyl alcohol, forms colourless, nacreous leaflets, m. p. 161°. Its aqueous solution reduces cold Fehling's solution. It condenses with benzaldehyde to form a *benzylidene* derivative, $C_{17}H_{22}O_3N_2$, which crystallises in glistening needles, m. p. 192—192·5°, is soluble in alkalis, but not in acids, and reduces Fehling's solution very slowly.

Ketomethoxyhydroxylaminodimethyltetrahydrobenzene oxime, $C_9H_{16}O_3N_2$, obtained from 2 : 4-dimethylquinol methyl ether, hydroxylamine, and methyl alcohol, forms glistening needles, m. p. 156·5—157°. Its behaviour towards Fehling's solution, acids, and alkalis is similar to that of the analogous ethoxy-compound just described. A. McK.

2 : 5 : 2′ : 5′-Tetramethoxystilbene. Hugo Kauffmann and Karl Burr (*Ber.*, 1907, **40**, 2358—2360).—2 : 5 : 2′ : 5′-*Tetramethoxystilbene*, $C_6H_3(OMe)_2\cdot CH:CH\cdot C_6H_3(OMe)_2$, formed by reduction with zinc dust and boiling alcoholic ammonia of the *product*, m. p. 123°, obtained on condensation of quinol dimethyl ether with chloral by means of concentrated sulphuric acid in glacial acetic acid solution cooled with ice, crystallises in light yellow needles, m. p. 99°, b. p. 140—180°/16 mm., and has a strong blue fluorescence. Whilst the exceptionally strong fluorescence of this substance is in agreement with Kauffmann's theoretical views, its yellow colour is of importance as proof that the methoxyl group is an auxochrome. G. Y.

Some *p*-Nitrobenzyl-mercaptals and -mercaptoles. A. Schaeffer and A. Murúa (*Ber.*, 1907, **40**, 2007—2008).—*p*-Nitrobenzyl mercaptan is a good qualitative reagent for ketones or aldehydes, and may be used to separate these substances. The condensation products obtained from it are well characterised, stable substances. The method of preparation consists in dissolving zinc *p*-nitrobenzyl mercaptide in alcohol saturated with hydrogen chloride and adding the calculated quantity of the aldehyde or ketone. After remaining for twenty-four hours at 0°, the products of condensation crystallise out. p-*Nitrobenzylethylidenemercaptal*, $CH_3\cdot CH(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, forms colourless, microscopic leaflets, m. p. 82°; p-*nitrobenzylsalicylidenemercaptal*, $C_{21}H_{18}O_5N_2S_2$, colourless prisms, m. p. 152°; p-*nitrobenzyl*-p-iso*propylbenzylidenemercaptal*, $C_{24}H_{24}O_4N_2S_2$, needles, m. p. 84°; p-*nitrobenzylphenylpropenylmercaptal*, $CHPh:CH\cdot CH(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, small prisms, m. p. 140°. Menthone yields the *mercaptole*, $C_{24}H_{30}O_4N_2S_2$, crystallising in small needles, m. p. 171°, and pulegone the corresponding *mercaptol*, $C_{24}H_{28}O_4N_2S_2$, m. p. 133°. p-*Nitrobenzylfurfurylidenemercaptal*, $C_{19}H_{14}O_5N_2S_2$, could not be obtained by the above method, but was prepared by boiling an alcohol solution of mercaptan and furfuraldehyde. It crystallises in leaflets, m. p. 87°. W. R.

Dibenzylideneacetone and Triphenylmethane. II. Distyrylchlorocarbinol. Fritz Straus and Fritz Caspari (*Ber.*, 1907, **40**, 2689—2709. Compare Straus and Ecker, Abstr., 1906, i, 859).—Moist silver oxide acting on distyryldichloromethane in ethereal solution replaces one of the chlorine atoms by hydroxyl, forming distyrylchlorocarbinol, $CCl(CH:CHPh)_2\cdot OH$, which bears the same relationship to the keto-chloride as triphenylcarbinol does to triphenylchloromethane. The chlorocarbinol forms colourless needles, m. p. 50°, and dissolves in concentrated sulphuric acid with a characteristic bluish-violet coloration. Hydrogen chloride or acetyl chloride reconvert it into distyryldichloromethane, whilst alcoholic hydrogen chloride or glacial acetic acid changes it to dibenzylideneacetone.

The elimination of hydrogen chloride could not be brought about even by such active reagents as pyridine, alcoholic potassium hydroxide, boiling alcoholic silver nitrate, or sodium acetate.

On heating for a time above the melting point at 60°, the chlorocarbinol is converted into an anhydride, $C_{34}H_{28}OCl_2$, crystallising in colourless needles, which sinter at 150°, m. p. 160°, and there is no elimination of hydrogen chloride.

The *methyl ether*, $CCl(CH{:}CHPh)_2{\cdot}OMe$, of the chlorocarbinol results when this is left standing with a little methyl alcohol. It crystallises in colourless, glistening plates or broad needles, m. p. 54—55°, and decomposes slowly on keeping. Concentrated sulphuric acid converts it into the sulphate, $CCl(CH{:}CHPh)_2{\cdot}OSO_3H$, which dissolves with the characteristic violet coloration. Methyl-alcoholic hydrogen chloride, in the cold or warm acetic acid, rapidly converts it into the ketone, but in the absence of mineral acids the methyl ether can be boiled with silver nitrate without changing. In benzene solution, hydrogen chloride regenerates the keto-chloride, chlorine being substituted for methoxyl.

Di-p-*chlorostyrylchlorocarbinol*, prepared in the manner already described for the monochloro-derivative, forms long, colourless needles, m. p. 101—102°, which become very electric when rubbed. It dissolves in concentrated sulphuric acid or liquid sulphur dioxide with an indigo-blue coloration and blood-red fluorescence, and shows all the reactions described for the monochlorocarbinol; the methyl ether has m. p. 94°, and is identical with the compound obtained by the action of sodium methoxide (compare Abstr., 1906, i, 859). The *anhydride* separates in glistening, colourless crystals, m. p. 165—167° (decomp.).

Benzophenone chloride, CPh_2Cl_2, and silver oxide, under the same conditions, form benzophenone, both chlorine atoms being eliminated.

The behaviour of the derivatives of distyrylchloromethane makes it necessary to regard them as triphenylmethane derivatives in which chlorine replaces a phenyl residue. E. F. A.

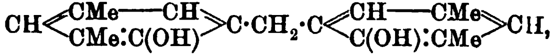
Cholesterol. IX. ADOLF WINDAUS (*Ber.*, 1907, 40, 2637—2639).—By heating cholesterol with sodium amyloxide in amyl alcohol solution for eight hours, an isomeric alcohol saturated towards bromine is produced. This is identical with the α-cholestanol obtained by Abderhalden and Diels and by Neuberg (Abstr., 1906, i, 272, 356), but as the substance is obtained from the amyloxide and is not obtainable by using energetic reducing agents, it is concluded that it is not a reduction product of cholesterol, an isomeric change having occurred which involves the formation of the ring compound, cylco*cholesterol*, $C_{27}H_{46}O$. This supports the conclusion previously arrived at, that the oxidation products of cholesterol are also ring compounds (this vol., i, 212).

W. R.

The Lederer-Manasse Synthesis of Phenol Alcohols. KARL AUWERS (*Ber.*, 1907, 40, 2524—2537).—The author has carried out a number of syntheses of phenol alcohols by the method given by

Lederer (Abstr., 1894, i, 577) and Manasse (Abstr., 1894, i, 575), and has studied the manner in which the course of the synthesis varies with the nature of the phenol employed and with the conditions of working.

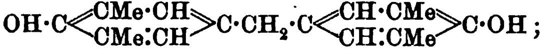
All his results confirm the observation made by the discoverers of the synthesis that the latter yields ortho- and para-, but not meta-, derivatives. The use of a strong alkali, such as sodium hydroxide, as condensing agent favours, at any rate with the homologous phenols, the formation of para-compounds. Thus the interaction of *p*-xylenol, sodium hydroxide, and formaldehyde at the ordinary temperature yields *p*-hydroxy-*ψ*-cumyl alcohol (Auwers and Ercklentz, Abstr., 1899, i, 35) in almost quantitative yield. In other cases, 50% or more of the para-derivative is obtained, and, at most, very small proportions of the isomeride. The action of the stronger alkalis differs also from that of the weaker ones, such as calcium hydroxide, in that the phenol alcohol formed is often accompanied by a larger or smaller quantity of a dihydroxydiphenylmethane derivative, which is less soluble in most solvents than the principal product (compare Manasse, Abstr., 1903, i, 28). Thus, by the action of formaldehyde and calcium hydroxide on as-*m*-xylenol at 50°, a good yield of *o*-hydroxymesityl alcohol [$\mathrm{OH : Me_2 : CH_2{\cdot}OH = 1 : 4 : 6 : 2}$] is generally obtained. In some cases, however, and especially if the heating is too intense or too prolonged, this alcohol is accompanied by 2 : 2′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetramethyldiphenylmethane*,



$$\mathrm{CH}{<}\begin{matrix}\mathrm{CMe{-\!-}CH}\\ \mathrm{CMe{:}C(OH)}\end{matrix}{>}\mathrm{C{\cdot}CH_2{\cdot}C}{<}\begin{matrix}\mathrm{CH{-\!-}CMe}\\ \mathrm{C(OH){:}CMe}\end{matrix}{>}\mathrm{CH},$$

which forms the main product when the condensation is effected by means of sodium hydroxide, even in very dilute solution. This compound crystallises from light petroleum in long, colourless needles, m. p. 145—146°, and gives no coloration with ferric chloride. Its *diacetyl* derivative, $C_{21}H_{24}O_4$, crystallises from aqueous alcohol in slender needles, m. p. 86°. This diphenylmethane derivative is probably formed by the action of the alkali on the phenolalcohol first formed (compare Auwers, Abstr., 1904, i, 487; also Kann, *Inaug. Diss., Marburg*, 1905, 22).

The nature of the phenol used has a still greater effect than that of the condensing agent in determining the formation of diphenylmethane derivatives. For instance, with *β*-naphthol, this synthesis yields dihydroxydinaphthylmethane as sole product. The same is the case with *m*-2-xylenol, which, when treated with formaldehyde and either sodium hydroxide or a weaker base, yields always 4 : 4′-*dihydroxy*-3 : 5 : 3′ : 5′-*tetramethyldiphenylmethane*,



$$\mathrm{OH{\cdot}C}{<}\begin{matrix}\mathrm{CMe{\cdot}CH}\\ \mathrm{CMe{:}CH}\end{matrix}{>}\mathrm{C{\cdot}CH_2{\cdot}C}{<}\begin{matrix}\mathrm{CH{\cdot}CMe}\\ \mathrm{CH{:}CMe}\end{matrix}{>}\mathrm{C{\cdot}OH};$$

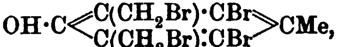
this compound, which is also formed by boiling *p*-hydroxymesitylpiperidine [$\mathrm{OH : Me_2 : CH_2{\cdot}C_5NH_{10} = 1 : 2 : 6 : 4}$] with dilute sodium hydroxide solution, crystallises from aqueous methyl alcohol in colourless, glassy needles, m. p. 175°, and when oxidised with chromic acid in acetic acid solution yields the xyloquinone described by Noelting and Baumann (Abstr., 1885, 892). Its *diacetyl* derivative, $C_{21}H_{24}O_4$, crystallises from methyl alcohol in slender needles, m. p. 142°.

The Lederer-Manasse synthesis fails in the cases of *p*-bromo-*o*-cresol and of other halogenated and nitro-phenols. This failure cannot be attributed to steric hindrance, but seems to depend on a specific chemical action of the halogens and the nitro-group, or possibly of any negative substituent.

The formation of dialdehydes from monohydric phenols by Reimer's synthesis takes place with difficulty, but the corresponding dihydric alcohols are readily formed from many simple phenols by means of the Lederer-Manasse synthesis. Thus when *p*-cresol is treated with formaldehyde and sodium hydroxide solution, it yields (1) *p*-homosaligenin and (2) 2 : 6-*dimethylol*-p-*cresol*, $OH{\cdot}C_6H_2Me(CH_2{\cdot}OH)_2$, which is identical with the compound, m. p. 133°, obtained by Lederer (Abstr., 1894, i, 577) from *p*-cresol and formaldehyde, and regarded by him as an isomeride of *p*-homosaligenin. The action of hydrogen bromide converts 2 : 6-dimethylol-*p*-cresol into vic.-*hydroxymesitylene dibromide* ($2^1 : 6^1$-*dibromomesitol*-1), $OH{\cdot}C_6H_2Me(CH_2Br)_2$, which crystallises from light petroleum in silky needles, m. p. 116—117°. Treatment of this dibromo-derivative with bromine yields, not as expected,

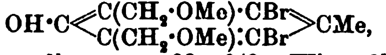
$$OH{\cdot}C_6Br_3(CH_2Br)_2\ [OH : Br_3 : (CH_2Br)_2 = 1 : 3 : 4 : 5 : 2 : 6]$$

(compare Auwers and Anselmino, Abstr., 1900, i, 159), but *dibromo*-vic.-*hydroxymesitylene bromide* ($3 : 5 : 2^1 : 6^1$-*tetrabromomesitol*-1),



$$\mathrm{OH{\cdot}C}\left<\begin{matrix}\mathrm{C(CH_2Br){\cdot}CBr}\\ \mathrm{C(CH_2Br){:}CBr}\end{matrix}\right>\mathrm{CMe},$$

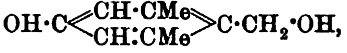
which crystallises from light petroleum in a felted mass of white needles, m. p. 152—152·5°. When boiled for a few minutes with methyl alcohol, this tetrabromo-derivative yields the *compound*,



$$\mathrm{OH{\cdot}C}\left<\begin{matrix}\mathrm{C(CH_2{\cdot}OMe){\cdot}CBr}\\ \mathrm{C(CH_2{\cdot}OMe){:}CBr}\end{matrix}\right>\mathrm{CMe},$$

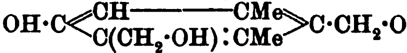
which separates in white, silky needles, m. p. 63—64°. When $2^1 : 6^1$-dibromomesitol-1 is heated on the water-bath with bromine and a little water, it is converted into tetrabromo-*p*-cresol ψ-bromide (compare Zincke and Wiederhold, Abstr., 1902, i, 284). In this case, contrary to what happens with about a dozen other phenols examined, the two side-chains in the ortho-position are removed, whilst that in the para-position remains.

With phenols containing both *o*- and *p*-hydrogen, the Lederer-Manasse reaction follows a very complicated course. This is also the case with phenols in which ortho substitution takes place relatively easily, as these yield, not only the two monohydric alcohols, but one or two dihydric alcohols and also diphenylmethane derivatives. Thus from the products of the interaction of *m*-xylenol, formaldehyde, and sodium hydroxide, the following compounds have been isolated: (1) p-*hydroxyhemimellithyl alcohol* (4-*hydroxy*-2 : 6-*dimethylbenzyl alcohol*),



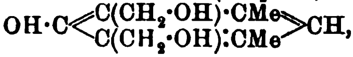
$$\mathrm{OH{\cdot}C}\left<\begin{matrix}\mathrm{CH{\cdot}CMe}\\ \mathrm{CH{:}CMe}\end{matrix}\right>\mathrm{C{\cdot}CH_2{\cdot}OH},$$

which crystallises from ethyl acetate in silky needles or from aqueous acetone in stout, rhombic plates, m. p. 174—175°. (2) A *dialcohol* of s-m-*xylenol*,



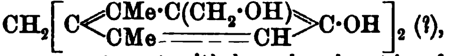
$$\mathrm{OH{\cdot}C}\left<\begin{matrix}\mathrm{CH\text{———}CMe}\\ \mathrm{C(CH_2{\cdot}OH){:}CMe}\end{matrix}\right>\mathrm{C{\cdot}CH_2{\cdot}OH}$$

or



$$\mathrm{OH{\cdot}C}\left<\begin{matrix}\mathrm{C(CH_2{\cdot}OH){\cdot}CMe}\\ \mathrm{C(CH_2{\cdot}OH){:}CMe}\end{matrix}\right>\mathrm{CH},$$

which crystallises from benzene in glassy prisms and leaflets, m. p. 138° (decomp.). (3) A *compound* of the formula



$$CH_2\left[C\begin{matrix}\diagup CMe\cdot C(CH_2\cdot OH)\diagdown \\ \diagdown CMe = = = = = CH \diagup\end{matrix}C\cdot OH\right]_2\ (?),$$

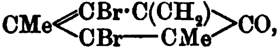
m. p. about 190°; on treatment with bromine in chloroform solution, it gives a tetrabromo-derivative, $CH_2[C_6BrMe_2(CH_2Br)\cdot OH]_2$, which crystallises from acetic acid in stellate aggregates of slender, shining needles, m. p. 232—234°. T. H. P.

Action of Bromine and Chlorine on Phenols. Substitution Products, ψ-Bromides, and ψ-Chlorides. XXI. o-ψ-Haloids and o-Methylenequinones from o-Oxymesityl Alcohol. KARL FRIES and K. KANN (*Annalen*, 1907, **353**, 335—356. Compare Zincke and Hedenström, this vol., i, 124; Auwers and Büttner, Abstr., 1899, i, 36).—The bromo-derivatives of *o*-hydroxybenzyl bromide resemble those of *p*-hydroxybenzyl bromide and are true ψ-bromides. The typical reactions take place, however, more slowly with the ortho- than with the para-compounds, and the intermediately formed methylenequinones have not been isolated, although such substances have been shown to be capable of existence by Fries and Hübner (Abstr., 1906, i, 190); the 1 : 2-naphthamethylenequinones studied by these authors differed from the *p*-methylenequinones described by Zincke in their indifference to additive reagents. As this difference might be caused by the naphthalene nucleus, the authors have studied the preparation of *o*-methylenequinones from *o*-hydroxymesityl alcohol, and found that 2 : 6-*dibromo*-1 : 3-*xylo*-4 : 5-*methylenequinone* is even more stable and indifferent than the 1 : 2-naphthamethylenequinones. These results render the formation of the *o*-methylenequinones as intermediate products in the transformations of the *o*-ψ-haloids extremely doubtful.

I. *Dibromo*-o-*hydroxymesityl Bromide and its Derivatives.*—Dibromo-*o*-hydroxymesityl ψ-bromide (Auwers, Abstr., 1906, i, 355) gives the reactions of the ψ-bromides, and is converted by the action of aqueous alkalis into an insoluble *product* which melts at high temperatures, and is probably a polymeride of *dibromo*-o-*methylenequinone*. *Dibromo*-o-*acetoxymesityl bromide*, $OAc\cdot C_6Br_2Me_2\cdot CH_2Br$, forms stout crystals, m. p. 130°. *Dibromo*-o-*mesityl alcohol*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OH$, crystallises in needles, m. p. 146°. The *methyl ether*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot OMe$, forms stout crystals, m. p. 66°.

The reduction of dibromo-*o*-hydroxymesityl bromide with zinc and hydrochloric acid leads to the formation of dibromomesitol and *tetrabromodi*-o-*hydroxydimesityl*, $OH\cdot C_6Me_2Br_2\cdot CH_2\cdot CH_2\cdot C_6Me_2Br_2\cdot OH$, which forms stout crystals, m. p. 261—262°. The *diacetate*, $C_{22}H_{22}O_4Br_4$, m. p. 245°. *Dibromomesityl acetate*, $C_{11}H_{12}O_2Br_2$, m. p. 103°.

2 : 6-*Dibromo*-1 : 3-*xylo*-5 : 4-*methylenequinone*,



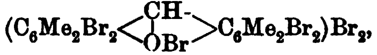
$$CMe\begin{matrix}\diagup CBr\cdot C(CH_2)\diagdown \\ \diagdown CBr — CMe \diagup\end{matrix}CO,$$

prepared by shaking dibromo-*o*-hydroxymesityl bromide in ethereal petroleum solution with 10% sodium acetate solution, crystallises in yellow prisms, m. p. 168°, and gives an intense brownish-red coloration with concentrated sulphuric acid. When reduced with zinc and hydrogen chloride in ethereal solution, it yields tetrabromodi-*o*-hydroxydimesityl.

II. *o-Hydroxymesityl Chloride and its Derivatives.*—*o-Hydroxymesityl ψ-chloride*, $OH{\cdot}C_6H_2Me_2{\cdot}CH_2Cl$, formed by the action of hydrogen chloride on *o*-hydroxymesityl alcohol in benzene solution, crystallises in long needles, m. p. 58°, yields the *o*-hydroxy-alcohol when treated with aqueous acetone, and when shaken in ethereal solution with sodium carbonate or acetate is converted into the *polymeride* of 1 : 3-xylo-5 : 4-methylenequinone, $(CH_2{:}C_6H_2Me_2{:}O)_3$, crystallising in white needles, m. p. 198—199°.

Di-2-hydroxydi-3 : 5-xylylmethane, $CH_2(C_6H_2Me_2{\cdot}OH)_2$, formed by boiling *o*-hydroxymesityl alcohol with 3% sodium hydroxide, or by boiling *as-m*-xylenol with formaldehyde and hydrochloric acid, crystallises in slender needles, m. p. 146°, and is readily soluble in aqueous alkalis. The *diacetate*, $C_{21}H_{24}O_4$, m. p. 86—87°.

The action of bromine on dihydroxydixylylmethane in chloroform solution leads to the formation of a crystalline *perbromide*,



$$(C_6Me_2Br_2{<}\overset{CH-}{\underset{OBr}{|}}{>}C_6Me_2Br_2)Br_2,$$

m. p. 190°, together with dibromo-*o*-hydroxymesityl bromide and a product which is soluble in alkalis and is probably a brominated xylenol.

When treated with nitrous acid, *o*-hydroxymesityl alcohol yields 5-nitro-1 : 3 : 4-xylenol, m. p. 78°, and a *substance*, $C_9H_{11}O_4N$, which crystallises in needles, m. p. 97°, and forms intensely red *alkali* salts and a *diacetate*, $C_{13}H_{15}O_6N$, m. p. 74°.

The action of nitrous acid on dibromo-*o*-hydroxymesityl alcohol leads to the formation of 2 : 6-*dibromo-5-nitro*-m-*4-xylenol*, $NO_2{\cdot}C_6Me_2Br_2{\cdot}OH$, which crystallises in yellow needles, m. p. 158°. The *acetate*, $C_{10}H_9O_4NBr_2$, m. p. 90°.

The carbinol group of *o*-hydroxymesityl alcohol is replaced by the nitro-group in the same manner by the action of fuming nitric acid.

G. Y.

Action of Bromine and Chlorine on Phenol. Substitution Products, ψ-Bromides, and ψ-Chlorides. XXII. *o*-ψ-Bromides and *o*-Methylenequinones from *o*-Hydroxy*iso*duryl Alcohol.

Theodor Zincke and C. von Hohorst (*Annalen*, 1907, **353**, 357—379).—*o*-Hydroxy*iso*duryl alcohol (4-ψ-cumenol-3-carbinol) behaves in the same manner as *o*-hydroxymesityl alcohol (see preceding abstract). In this case the halogen-free quinone, *o-isodurylenequinone* has been obtained.

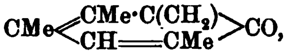
ψ-Cumenol alcohol (Manasse, Abstr., 1903, i, 28) yields a *nitro*-derivative when treated with sodium nitrite in glacial acetic acid solution; the *diacetate*, $C_{14}H_{18}O_4$, crystallises in flat needles, m. p. 50·5—51·5°. When boiled with 5% sodium hydroxide, the alcohol yields *di-*o*-ψ-cumenolmethane*, $CH_2(C_6HMe_3{\cdot}OH)_2$, which is formed also by the action of formaldehyde and alcoholic hydrogen chloride on ψ-cumenol. It crystallises in white needles, m. p. 171—172°, forms a sparingly soluble *alkali* salt, and yields a deep red *perbromide*. The *diacetate*, $C_{23}H_{28}O_4$, crystallises in small leaflets, m. p. 130—131°.

o-*Hydroxyisoduryl ψ-bromide*, $OH\cdot C_6HMe_3\cdot CH_2Br$, formed by the action of hydrogen bromide on the alcohol in benzene solution, crystallises in white needles, m. p. 107—107·5°, gives a yellow coloration when heated with alkalis, and is converted by boiling, more slowly by cold, water into *o*-ψ-cumenolmethane and formaldehyde, or by dilute alkalis in ethereal solution into the methylenequinone, or by acetic anhydride into the diacetate of *o*-hydroxy*iso*duryl alcohol.

o-*Hydroxyisoduryl ψ-chloride*, $C_{10}H_{13}OCl$, crystallises in white needles, m. p. 99—100°, and gives the same reactions as the ψ-bromide.

o-*Acetoxyisoduryl ψ-bromide*, $OAc\cdot C_6HMe_3\cdot CH_2Br$, forms white needles, m. p. 127—128°. The *ψ-chloride* crystallises in white needles, m. p. 116—117°.

o-*Hydroxyisoduryl methyl ether*, $C_{11}H_{16}O_2$, crystallises in stout, colourless needles, m. p. 44—45°; the *acetate* is an oil. o-*Hydroxyisoduryl acetate* forms white needles, m. p. 57—58°.

When shaken in ethereal solution with dilute alkalis, the ψ-bromide yields o-*isodurylenequinone*  $\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe\cdot C(CH_2)}\\ \mathrm{CH{=\!=}CMe}\end{matrix}{>}\mathrm{CO}$, and its *polymeride*, $(C_{10}H_{12}O)_3$. The *quinone* crystallises in yellow, monoclinic prisms, m. p. 128—129°, gives a deep red coloration with concentrated sulphuric acid, does not react with methyl alcohol, glacial acetic acid, acetic anhydride, alkalis in acetone solution, or hydrogen bromide in glacial acetic acid solution, and when exposed in solution to sunlight is gradually converted into its *polymeride*. This crystallises in colourless, rhombic plates, m. p. 173—174°, and is indifferent to the action of reagents.

6-*Bromo*-o-*hydroxyisoduryl ψ-bromide*, $OH\cdot C_6Me_3Br\cdot CH_2Br$, formed by the action of bromine on *o*-hydroxy*iso*duryl alcohol in chloroform solution, crystallises in white needles, m. p. 111—112°, and is not identical with Auwer's compound (Abstr., 1906, i, 354). The *acetate* of the ψ-bromide, $C_{12}H_{14}O_2Br_2$, forms needles or leaflets, m. p. 135—136°. The *diacetate*, $OAc\cdot C_6Me_3Br\cdot CH_2\cdot OAc$, crystallises in white needles, m. p. 88—88·5°. 6-*Bromo*-o-*hydroxyisoduryl acetate*,

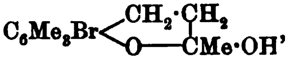
$$OH\cdot C_6Me_3Br\cdot CH_2\cdot OAc,$$

crystallises in rhombic plates, m. p. 91—92°, and is insoluble in alkalis. The *methyl ether*, $OH\cdot C_6Me_3Br\cdot CH_2\cdot OMe$, crystallises in white needles, m. p. 94—94·5°, and forms an *acetate*, $C_{13}H_{17}O_3Br$, crystallising in stout needles, m. p. 63—64°.

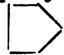
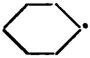
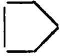
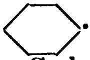
When shaken in ethereal solution with dilute sodium hydroxide, the ψ-bromide yields 6-*bromo*-o-*isodurylenequinone*, $CH_2{:}C_6Me_3Br{:}O$, and its *polymeride*, $(C_{10}H_{11}OBr)_3$. The *quinone* crystallises in white needles, m. p. 142—142·5°. The *polymeride* crystallises in yellowish-white needles, m. p. 255—257°. The quinone and its polymeride are completely unreactive.

The action of acetone and water on the ψ-bromide leads to the formation of 6-*bromo*-o-*hydroxyisoduryl alcohol* and, as the main product, a *condensation product* of the alcohol with acetone.

6-*Bromo*-o-*hydroxyisoduryl alcohol*, $OH\cdot C_6Me_3Br\cdot CH_2\cdot OH$, crystallises in small, white needles, m. p. 128—129°.

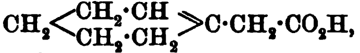
The *condensation product*,  $C_6Me_3Br{<}\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CMe\cdot OH\end{matrix}$, forms stout prisms or rhombohedra, m. p. 81—82°, and yields an *acetate*, $C_{15}H_{19}O_3Br$, crystallising in white needles, m. p. 86—87°. G. Y.

Terpenes and Ethereal Oils. LXXXIV. Carboxylic Acids of Cyclic Hydrocarbons and their Transformation Products.

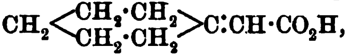
OTTO WALLACH (*Annalen*, 1907, **353**, 284—317. Compare this vol., i, 541).—Acids and bases which are derived from the simplest cyclic hydrocarbons and have the carboxyl and amino-groups respectively situated in a side-chain are but little known. The present work was undertaken to fill this gap in our knowledge. The author proposes the term cyclyl for the univalent groups, *cyclo*pentyl, *cyclo*hexyl, corresponding to the *cyclo*hydrocarbons; thus $\cdot CH_2\cdot CO_2H$, $\cdot CH_2\cdot CO_2H$, &c., are cyclylacetic acids, whilst $\cdot CH_2\cdot NH_2$, $\cdot CH_2\cdot NH_2$, &c., are cyclylmethylamines.

Cyclylacetic acids and their homologues are prepared readily by condensation of cyclic ketones with ethyl bromoacetate and its homologues, treatment of the resulting hydroxy-ester with hydrogen bromide, and reduction of the bromo-ester, so obtained, or of the corresponding bromo-acid. The cyclylacetic acids yield amides, from which are obtained the cyclylmethylamines directly by Hofmann's reaction, or the cyclylethylamines by conversion into, and reduction of, the cyclylacetonitriles.

I. *Compounds from* cyclo*Hexanone; Isomeric* cyclo*Hexeneacetic Acids.*—It is found that, on loss of water, *cyclo*hexanolacetic acid (Wallach and Isaac, Abstr., 1906, i, 564) yields two *cyclo*hexeneacetic acids; one of these, m. p. 38°, which has been described previously (Abstr., 1906, i, 176), has the constitution



$$CH_2{<}\begin{matrix}CH_2\cdot CH\\ CH_2\cdot CH_2\end{matrix}{>}C\cdot CH_2\cdot CO_2H,$$

whilst the new isomeride, m. p. 91—92°, is Δ^{α}-cyclo*hexeneacetic acid*,  $CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CH\cdot CO_2H$, since on oxidation with potassium permanganate it yields *cyclo*hexanone; it crystallises in long needles and distils slowly in a current of steam. Both *cyclo*hexeneacetic acids yield a *hydrobromide*, m. p. 89—90°. 1 : α-*Dibromo*cyclo*hexylacetic acid*, $C_8H_{12}O_2Br_2$, m. p. 133—134°, formed from Δ^{α}-*cyclo*hexeneacetic acid, is converted into an oil by the action of alkali carbonates. 1-*Chloro*cyclo*hexylacetic acid*, $C_6H_{10}Cl\cdot CH_2\cdot CO_2H$, separates from methyl alcohol in crystals, m. p. 83°. 1-*Iodo*cyclo*hexylacetic acid*, $C_8H_{13}O_2I$, forms transparent prisms, m. p. 99—100° (becoming brown).

The oil, b. p. 178—185°, formed by the action of sodium carbonate on 1 : 2-dibromo*cyclo*hexylacetic acid, distils in a current of steam and is probably a brominated lactone (compare Abstr., 1906, i, 176). A *lactone* is obtained also when Δ^1-*cyclo*hexeneacetic acid is boiled with sulphuric acid. These properties confirm its constitution as a $\beta\gamma$-unsaturated acid. Δ^1-cyclo*Hexeneacetamide*, $C_6H_9{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, prepared by the successive action of phosphorus pentachloride and ethereal ammonia on the acid, separates from methyl alcohol in crystals, m. p. 152—153°.

The product, $C_7H_{10}O$, b. p. 175°, obtained on oxidation of Δ^1-*cyclo*hexeneacetic acid (Abstr., 1906, i, 176), is now considered to be an aldehyde; when purified by conversion into its *semicarbazone*, $C_8H_{13}ON_3$, m. p. 203—204°, and liberation by means of oxalic acid, it has an odour of benzaldehyde, reduces silver oxide in boiling water, and is oxidised by chromic and sulphuric acids, yielding glutaric acid. Since the semicarbazone of 2-methyl-Δ^2-*cyclo*hexenone has m. p. 211—212°, and that of Δ^1-tetrahydrobenzaldehyde has m. p. 212—213°, the constitution of the aldehyde from the *cyclo*hexeneacetic acid requires further investigation.

cyclo*Hexylacetic acid*, $C_6H_{11}{\cdot}CH_2{\cdot}CO_2H$, prepared by the action of hydrogen bromide on ethyl *cyclo*hexanolacetate and treatment of the product with zinc dust, is freed from unsaturated acids by oxidation of the latter with potassium permanganate; it solidifies when cooled, m. p. 30—31°, b. p. 245—247°. The *silver* salt, $C_8H_{13}O_2Ag$, is sparingly soluble. The *amide*, $C_7H_{13}{\cdot}CO{\cdot}NH_2$, m. p. 168°, crystallises from dilute methyl alcohol. The *nitrile*, $C_6H_{11}{\cdot}CH_2{\cdot}CN$, b. p. 215—217°, distils with steam, and on reduction yields *β-aminoethyl*-cyclo*hexane*, $C_6H_{11}{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, b. p. 188—189°. The *hydrochloride*, m. p. 252—253°; the *platinichloride* decomposes at 253—254°; the *carbamide*, $C_8H_{15}{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 85—86°; the *trimethylammonium iodide*, $C_8H_{15}{\cdot}NMe_3I$, m. p. 221—222°.

*cyclo*Hexanemethylamine, $C_6H_{11}{\cdot}CH_2{\cdot}NH_2$, b. p. 162—164° (Demjanoff, Abstr., 1904, i, 410), formed by the action of bromine and potassium hydroxide on the acetamide, absorbs carbon dioxide yielding a solid *carbonate*; the *hydrochloride*, m. p. above 210°; the *carbamide*, $C_7H_{13}{\cdot}NH{\cdot}CO{\cdot}NH_2$, m. p. 225°.

Ketones from cyclo*Hexylacetic Acid.—Dihexahydrobenzyl ketone*, $CO(CH_2{\cdot}C_6H_{11})_2$, formed by distilling calcium *cyclo*hexylacetic acid at 120—130° under reduced pressure, solidifies at low temperatures, is an oil at the ordinary temperature, and has a feeble odour. The *semicarbazone*, $C_{16}H_{29}ON_3$, m. p. 142—145°.

Hexahydrobenzyl methyl ketone, b. p. 198—200°, formed from *cyclo*hexylacetic acid, may be identical with Freundler's ketone (Abstr., 1906, i, 283); the semicarbazone, m. p. 165—166° (182·5°: Freundler, *loc. cit.*).

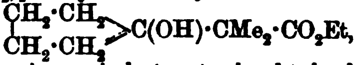
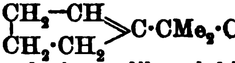
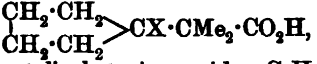
II. *Compounds from Suberone.*—cyclo*Heptylacetic acid*,

$$C_7H_{13}{\cdot}CH_2{\cdot}CO_2H,$$

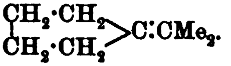
prepared by the successive action of hydrogen bromide and zinc dust on ethyl suberolacetate (Abstr., 1901, i, 156), is obtained as an oil, b. p. 165°/19 mm.; the *silver* salt, $C_9H_{15}O_2Ag$, is sparingly soluble. cyclo*Heptylacetamide*, $C_7H_{13}{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, crystallises in leaflets, m. p. 146—148°. cyclo*Heptanemethylamine*, $C_7H_{13}{\cdot}CH_2{\cdot}NH_2$, b. p. 193—195°, $D^{21\cdot5}$ 0·8840, n_D 1·4719, absorbs carbon dioxide and volatilises slowly with ether. The *hydrochloride*, m. p. 229—232°; the *platinichloride*, $(C_8H_{18}N)_2PtCl_6$, was analysed; the *carbamide*,

$C_7H_{13}\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, crystallises in leaflets, m. p. 127—129°; the *trimethylammonium iodide*, $C_8H_{15}\cdot NMe_3I$, m. p. 223°.

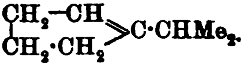
III. *Compounds from* cyclo*Pentanone*.—[With Karl Fleischer.]—*cyclo*Pentylacetic acid, $C_5H_9\cdot CH_2\cdot CO_2H$, prepared from ethyl *cyclo*pentanolacetate (Wallach and Speranski, Abstr., 1902, i, 800), is obtained as an oil, b. p. 226—230° (139—140°/26 mm.: Verwey, Abstr., 1896, i, 671), and has an odour resembling that of the fatty acids. The *amide*, $C_5H_9\cdot CH_2\cdot CO\cdot NH_2$, m. p. 143—145°. cyclo*Pentanemethylamine*, $C_5H_9\cdot CH_2\cdot NH_2$, b. p. 139—145°, absorbs carbon dioxide and is readily soluble in water; the *hydrochloride* is deliquescent; the *platinichloride*, $(C_6H_{14}N_2)_2PtCl_6$, was analysed.

Ethyl cyclo*pentanol*iso*butyrate*,  $\left.\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\right>C(OH)\cdot CMe_2\cdot CO_2Et$, formed from *cyclo*pentanone and ethyl α-bromo*iso*butyrate, is obtained as an oil, b. p. 108—113°/11 mm., containing small amounts of the unsaturated *ester*, into which it is converted completely when heated with potassium hydrogen sulphate at 150—160°. This on hydrolysis yields cyclo*pentene*iso*butyric acid*,  $\left.\begin{array}{l}CH_2-CH\\ CH_2\cdot CH_2\end{array}\right>C\cdot CMe_2\cdot CO_2H$, b. p. 148—150°/27 mm.; the *ammonium* salt is readily soluble; the *silver* salt, $C_9H_{13}O_2Ag$, was analysed. The unsaturated acid forms crystalline additive products,  $\left.\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\right>CX\cdot CMe_2\cdot CO_2H$, with hydrogen haloids. 1-*Chloro*cyclo*pentyl*iso*butyric acid*, $C_9H_{15}O_2Cl$, m. p. 122·5—123·5°. 1-*Bromo*cyclo*pentyl*iso*butyric acid*, m. p. 113—114° (decomp.). 1-*Iodo*cyclo*pentyl*iso*butyric acid*, m. p. 107—108° (decomp.).

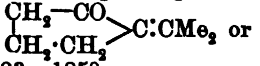
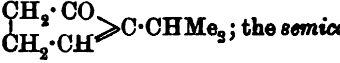
When distilled under atmospheric pressure, *cyclo*penteneisobutyric acid yields a *hydrocarbon*, b. p. 136—137°, D^{20} 0·817, n_D 1·4581, which is probably a mixture of I with a small amount of II. With nitrosyl chloride it forms an intense blue oil, which is volatile

I. 

$$\left.\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\right>C{:}CMe_2.$$

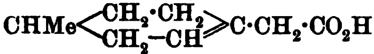
II. 

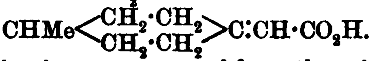
$$\left.\begin{array}{l}CH_2-CH\\ CH_2\cdot CH_2\end{array}\right>C\cdot CHMe_2.$$

with steam, and on oxidation with potassium permanganate yields *cyclo*pentanone and a crystalline *glycol*, m. p. 61—63°. When heated with alcoholic sulphuric acid on the water-bath, the hydrocarbon I is transformed into II. This forms a crystalline *additive product*, $C_8H_{14}NOCl$, with nitrosyl chloride, which on conversion into the corresponding *oxime* and subsequent hydrolysis yields a *ketone*,  $\left.\begin{array}{l}CH_2-CO\\ CH_2\cdot CH_2\end{array}\right>C{:}CMe_2$ or  $\left.\begin{array}{l}CH_2\cdot CO\\ CH_2\cdot CH\end{array}\right>C\cdot CHMe_2$; the *semicarbazone*, m. p. 183—185°.

The semicarbazone of *cyclo*pentanone, m. p. 205—206° if heated slowly, but m. p. 212—213° if heated rapidly.

IV. *Compounds from* 1-*Methyl*cyclo*hexane*-4-*one*.—[With Edgar Evans.]—Since the crude 1-methyl*cyclo*hexeneacetic acid, formed from 1-methyl*cyclo*hexane-4-one (Abstr., 1906, i, 566), might be a mixture of the two acids I and II, it was examined successfully for Perkin and Pope's acid, m. p. 70—71° (Proc., 1906, 22, 107). On oxidation with potassium permanganate, the crude acid yielded 1-methyl*cyclo*hexane-4-ol, whilst the acid, m. p. 42—43°, purified by distillation in a current of steam, yielded 1-methyl*cyclo*hexane-4-one. The acid, m. p. 42—43°, is considered to have the constitution II (compare Marckwald and Meth, Abstr., 1906, i, 360, 584, 663).

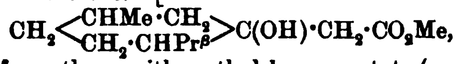
I. 
$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2-CH}\end{matrix}{\gg}\mathrm{C\cdot CH_2\cdot CO_2H}$$

II. 
$$\mathrm{CHMe}{<}\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}{>}\mathrm{C{:}CH\cdot CO_2H.}$$

The following derivatives are prepared from the acid, m. p. 42—43°.

4-*Chloro*-1-*methyl*cyclo*hexyl*-4-*acetic acid*, $C_9H_{15}O_2Cl$, m. p. 88—89°. 4-*Bromo*-1-*methyl*cyclo*hexyl*-4-*acetic acid*, m. p. 85—86°, yields the acid, m. p. 41—42°, when heated with sodium methoxide solution. 3 : 4-*Dibromo*-1-*methyl*cyclo*hexyl*-4-*acetic acid*, m. p. 97—99°. 1-*Methyl*cyclo*hexyl*-4-*acetamide*, $C_9H_{15}ON$, m. p. 155—156°. The *nitrile*, b. p. 107°/15 mm.

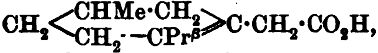
1-*Methyl*cyclo*hexyl*-4-*acetic acid*, $C_6H_{10}Me\cdot CH_2\cdot CO_2H$, formed in the same manner as *cyclo*hexyl-1-acetic acid, separates from methyl alcohol in crystals, m. p. 63—65°; the *amide*, $C_6H_{10}Me\cdot CH_2\cdot CO\cdot NH_2$, m. p. 161—162°.

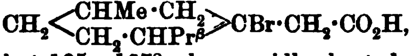
V. *Compounds from Menthone.*—[With EDUARD SCHELLACK.]—*Methyl mentholacetate*,  $\mathrm{CH_2}{<}\begin{matrix}\mathrm{CHMe\cdot CH_2}\\ \mathrm{CH_2\cdot CHPr^{\beta}}\end{matrix}{>}\mathrm{C(OH)\cdot CH_2\cdot CO_2Me}$, prepared by condensation of menthone with methyl bromoacetate (compare Wallach and Thölke, Abstr., 1902, i, 799), readily forms crystals, m. p. 32—33°, b. p. 136—137°/10 mm.; the *acid*,

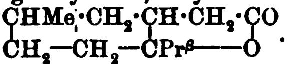
$$C_6H_8MePr^{\beta}(OH)\cdot CH_2\cdot CO_2H,$$

m. p. 82—83°, b. p. 193—197°/11 mm.

Mentheneacetic acid (*loc. cit.*) has the constitution


$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CHMe\cdot CH_2}\\ \mathrm{CH_2-CPr^{\beta}}\end{matrix}{\gg}\mathrm{C\cdot CH_2\cdot CO_2H,}$$

since on oxidation it yields only traces of menthone. When treated with hydrogen bromide in glacial acetic acid solution, it forms *bromomenthaneacetic acid*,  $\mathrm{CH_2}{<}\begin{matrix}\mathrm{CHMe\cdot CH_2}\\ \mathrm{CH_2\cdot CHPr^{\beta}}\end{matrix}{>}\mathrm{CBr\cdot CH_2\cdot CO_2H}$, m. p. 126—130° when slowly, but 135—137° when rapidly, heated.

A lævorotatory, liquid *lactone*, $C_{12}H_{20}O_2$, b. p. 300—305°, D 1·015, n_D^{22} 1·4781, is obtained together with mentheneacetic acid by heating ethyl mentholacetate with potassium hydrogen sulphate and hydrolysing the resulting unsaturated ether. When boiled with hydrogen iodide and red phosphorus in glacial acetic acid solution, it is converted into a dextrorotatory, crystalline *modification*, m. p. 88·5—89·5°. As both substances dissolve when boiled with alkalis and are reprecipitated unchanged by acids, they are considered to be modifications of the γ-lactone,  $\begin{array}{l}\mathrm{CHMe\cdot CH_2\cdot CH\cdot CH_2\cdot CO}\\ \mathrm{CH_2-CH_2-CPr^{\beta}-\!\!-O}\end{array}$.

Menthaneacetic acid, $C_6H_9MePr^{\beta}\cdot CH_2\cdot CO_2H$, formed by reduction of ethyl bromomenthaneacetate, is an oil, b. p. 166—170°/11 mm.; the *amide*, $C_{11}H_{21}\cdot CO\cdot NH_2$, m. p. 148—150°. G. Y.

Sulphonation in Presence of Mercury. OTTO DIMROTH and WOLFGANG VON SCHMAEDEL (*Ber.*, 1907, **40**, 2411—2415. Compare Abstr., 1899, i, 54, 428; 1901, i, 439; 1902, i, 656, 849; Iljinsky, Abstr., 1904, i, 176; Schmidt, *ibid.*, 256; Liebermann and Pleus, *ibid.*, 326; Farbenfabriken vorm. F. Bayer and Co., Abstr., 1906, i, 293).—This work was undertaken with the object of determining the nature of the influence of small amounts of mercury in the sulphonation of anthraquinone and in similar reactions. Contrary to the statement of Holdermann (Abstr., 1906, i, 439), it is found that whilst the sulphonation of benzoic acid in absence of mercury leads to the formation of the meta- and para-derivatives only, the reaction is accelerated and the ortho-derivative also is formed in small amount if mercuric sulphate is added to the reacting mixture. It is found further that *o*-hydroxymercuribenzoic anhydride yields *o*-sulphobenzoic acid, together with small amounts of the meta- and para-compounds, when treated at the ordinary temperature with sulphuric acid containing 18% of sulphur trioxide. It is concluded that in the sulphonation of benzoic acid by means of concentrated sulphuric acid in presence of mercury, the following reactions take place: (1) formation of *o*-carboxyphenylmercuric sulphate, $CO_2H\cdot C_6H_4\cdot Hg\cdot SO_4H$, which is limited by equilibrium with the reverse reaction; (2) formation of benzoic acid and mercuric sulphate; (3) conversion of *o*-carboxyphenylmercuric sulphate by sulphuric acid into *o*-sulphobenzoic acid and mercuric sulphate, and (4) direct sulphonation of benzoic acid in the meta- and para-positions. G. Y.

Bimolecular Anhydrides of Anthranilic Acid. GEORG SCHROETER (*Ber.*, 1907, **40**, 2628—2630).—When the yellow anhydride of anthranoylanthranilic acid (this vol., i, 529) is warmed with benzenesulphonyl chloride, or benzenesulphonylanthranoylanthranilic acid with thionyl chloride, the anhydride of benzenesulphonylanthranoylanthranilic acid, m. p. 214—215°, is obtained, which yields the acid, m. p. 222°, by treatment with alkalis. These two compounds are identical with those prepared by Heller (Abstr., 1904, i, 160).

Pawlewski's *N*-phenylsulphoneanthranilic acid (Abstr., 1905, i, 437) is identical with the author's benzenesulphonylanthranilic acid (*loc. cit.*), the m. p. of which is 214° and not 223°. C. S.

3-Nitro-4-dimethylaminobenzoic Acid. FRÉDÉRIC REVERDIN (*Arch. Sci. phys. nat.*, 1907, [iv], **23**, 458—466; *Ber.*, 1907, **40**, 2442—2448).—The nitration of dimethylaminobenzoic acid with 30% nitric acid at 30° yields, in addition to 3-nitro-4-dimethylaminobenzoic acid and 2:4-dinitrodimethylaniline already described by Steiner, some 2:4-dinitromethylaniline. On nitrating the acid by means of a mixture of nitric and sulphuric acids, the author also obtained some *p*-nitrodimethylaniline, m. p. 161—162°. Nitration in glacial acetic acid solution yields a mixture of 2:4-dinitromethylaniline, 2:4:6-trinitrodimethylaniline, and two other substances melting at 179° and 164° respectively which were not identified; on a subsequent occasion, nitration under apparently similar conditions yielded a substance which did not melt at 240° and appeared to be nitromethylaminobenzoic acid. The nitration of nitrodimethylaminobenzoic acid by means of nitric and sulphuric acids yields Romburgh's trinitrophenylmethylnitroamine (compare Abstr., 1885, 660), which, according to the present author, melts at 129° instead of 127°, and a substance melting at 193° which is probably trinitrodimethylaminobenzoic acid.

P. H.

Triphenylamine and Triphenylamine-*o*-carboxylic Acid (Diphenylanthranilic Acid). IRMA GOLDBERG and MARIE NIMEROVSKY [in part, R. MAAG] (*Ber.*, 1907, **40**, 2448—2452).—Since phenylanthranilic acid is readily obtained by the interaction of anthranilic acid and bromobenzene in the presence of copper as a catalyst (Goldberg, Abstr., 1906, i, 426), attempts were made to replace the remaining imino-hydrogen atom by another phenyl group. This was found to be possible when iodobenzene was used instead of bromobenzene, *diphenylanthranilic acid*, $NPh_2\cdot C_6H_4\cdot CO_2H$, being obtained. This acid forms sulphur-yellow, feathery crystals, m. p. 208°; when heated above its melting point, it is converted quantitatively into triphenylamine with the liberation of carbon dioxide. Triphenylamine may also be prepared from diphenylamine and iodobenzene by the use of copper as a catalyst.

10-*Phenylacridone*, $C_{13}H_8ONPh$, obtained by heating diphenylanthranilic acid with concentrated sulphuric acid at 100°, forms yellow crystals, m. p. 276° (corr.). Its solutions in amyl alcohol, benzene, and toluene are not fluorescent, whilst the acetic acid solution shows an intense blue fluorescence.

Phenyl-p-*tolylanthranilic acid*, $C_7H_7\cdot NPh\cdot C_6H_4\cdot CO_2H$, a yellow powder, m. p. 175°, has also been prepared by the above method.

W. H. G.

Calcium *p*-Hydroxybenzoate. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1907, **144**, 1118—1119. Compare this vol., i, 532).—On treating anhydrous calcium *p*-hydroxybenzoate with a small quantity of water at 15°, the crystalline monohydrate is formed. When the anhydrous salt is shaken with excess of water, it slowly dissolves and at the moment before the dissolution of the last crystalline spangles the phenomenon of triboluminescence is observed.

The 3% solution at 17° when first prepared is turbid, but it afterwards becomes quite clear. Such a solution when kept in a closed vessel overnight (during which the temperature fell to 5° and then rose to 14°) separated into two layers, of which the upper one remained clear and contained the monohydrate, whilst the lower one consisted of an emulsion of a perhydrated salt. After a time, dilute, clear solutions of calcium *p*-hydroxybenzoate deposit a salt of a spongy, flocculent appearance. This is quite insoluble and is a mixture of several hydrates of an allotropic salt, the trihydrate apparently predominating. The densities of solutions of calcium *p*-hydroxybenzoate in water are 0·5% $D^{16}=0·993$, 0·8% $D^{16}=0·9973$, 1% $D^{18}=1·0024$, 1·5% $D^{15}=1·0065$, 2% $D^{18}=1·0138$, 2·5% $D^{18}=1·0156$; in ethyl alcohol (95%), 0·5% $D^{16}=0·8128$, 1% $D^{18·5}=1·0147$.

E. H.

6-Hydroxy-4-methylcoumarin and β-Quinoylcrotonic Acid. WALTHER BORSCHE (*Ber.*, 1907, 40, 2731—2736).—Pechmann (Abstr., 1901, i, 285, 286) found that his method of synthesis of coumarin derivatives from the esters of β-ketonic acids and phenols failed in the case of quinol. This has been repeated, and under suitable conditions quinol and ethylacetoacetate react in presence of concentrated sulphuric acid forming 6-*hydroxy*-4-*methylcoumarin*, a faintly yellow, crystalline substance, m. p. 243°.

The *acetate* crystallises in long, colourless needles, m. p. 137—138°, whilst the 5 : 7-*dibromo*-derivative forms colourless needles, m. p. 202—203°.

7(?)-*Nitro*-6-*hydroxy*-4-*methylcoumarin* separates from alcohol in yellow, flat needles, m. p. 210° (decomp.), and forms a *benzoate* crystallising in colourless needles, m. p. 166—167 ; the 5 : 7-*dinitro*-compound forms orange-yellow needles, m. p. 219°.

Quinol reacts less readily with ethyl α-methylacetoacetate and yields only small quantities of 3 : 4-*dimethyl*-6-*hydroxycoumarin*, which crystallises in colourless plates, m. p. 235—236°. Quinol does not react with ethylbenzoyl acetate.

6-Hydroxy-4-methylcoumarin is converted by the action of zinc dust and sodium hydroxide into 2 : 5-*dihydroxy*-β-*methylcinnamic acid*, $C_6H_3(OH)_2\cdot CMe{:}CH\cdot CO_2H$, separating in faintly brown-coloured, round, crystalline aggregates, m. p. 155—156°. On oxidation with chromic acid it is converted into β-*quinoylcrotonic acid*,

$$C_6H_3O_2\cdot CMe{:}CH\cdot CO_2H,$$

crystallising in orange needles, m. p. 167—168°. The β-*dianilino*-derivative forms dark bluish-red, glistening needles, m. p. 232° (decomp.); the β-*oximino*-derivative crystallises in yellow needles, m. p. 179—180° (decomp.), and the *phenylcarbamic acid hydrazone* is a red, crystalline powder, m. p. 150° (decomp.). E. F. A.

Hydroxyamino-Acids. ERNEST FOURNEAU (*Bull. Soc. chim.*, 1907, [iv], 1, 549—558. Compare Abstr., 1904, i, 377).—*Dimethylaminophenyl-lactic acid*, $OH\cdot CHPh\cdot CH(NMe_2)\cdot CO_2H$, m. p. 145°, obtained by heating phenylchlorolactic acid with dimethylamine, dissolved in benzene, in a closed tube, crystallises in cubes, is insoluble in acetone and chloroform, and neutral to litmus. It decomposes at 150°, passing into a new *substance*, which itself decomposes at 205° (approx.). The *sodium* and *copper* salts are crystalline, but the second of these appears to have an abnormal constitution analogous to that of the copper derivative of *iso*serine described by Fischer (Abstr., 1902, i, 269). The *methyl ester hydrochloride*, m. p. 175° (decomp.), prepared in the usual way, crystallises from alcohol in silky needles. The *ethyl ester*, b. p. 170—171°/24 mm., yields a *hydrochloride*, m. p. 197°, which crystallises in slender needles. The *aurichloride*, m. p. 162°, forms yellow spangles; the *platinichloride* decomposes at 203°; the *benzoyl* derivative, m. p. 172—173°, crystallises in silky needles. When methyl or ethyl phenylchlorolactate is heated with excess of dimethylamine, dissolved in benzene, in a closed tube, the *dimethylamide* of dimethylaminophenyl-lactic acid, $OH\cdot CHPh\cdot CH(NMe_2)\cdot CO\cdot NMe_2$, m. p. 148°, is produced. This is crystalline, readily soluble in alcohol or chloroform, slightly so in ether or water, and is strongly basic. The *hydrochloride*, m. p. 210°, forms short, prismatic crystals. The *platinichloride*, m. p. 118°, forms slender, red needles, and the *aurichloride*, m. p. 81°, canary-yellow crystals. The *benzoyl* derivative, m. p. 156°, separates from acetone in tabular crystals; the *hydrochloride* of this forms silky tufts, m. p. 200° (decomp.), of acid reaction and bitter taste, and the *platinichloride*, m. p. 180°, bright red spangles.

When the amine is not used in excess, there are also formed some *dimethylamide* of phenylchlorolactic acid and some ethyl phenylglycidate. The former has m. p. 140°, separates from dilute alcohol in large leaflets, and is insoluble both in acids and bases. When warmed with a concentrated solution of potassium hydroxide, it decomposes, yielding dimethylamine, and, when heated in a closed tube at 130° with dimethylamine, passes into the dimethylamide of phenyldimethylaminolactic acid.

The *diethylamide* of diethylaminophenyl-lactic acid,

$$OH{\cdot}CHPh{\cdot}CH(NEt_2){\cdot}CO{\cdot}NEt_2,$$

prepared similarly, has m. p. 92—93°, and separates from a mixture of ether and light petroleum in long, silky needles. The *diethylamide* of phenylchlorolactic acid, obtained when diethylamine is not used in excess, has m. p. 149°, and crystallises from a mixture of alcohol and ether in slender needles.

The *methylamide* of methylaminophenyl-lactic acid,

$$OH{\cdot}CHPh{\cdot}CH(NHMe){\cdot}CO{\cdot}NHMe,$$

obtained by the action of methylamine dissolved in benzene on ethyl phenylchlorolactate, separates from acetone in slender, silky needles, m. p. 153°. The *hydrochloride*, m. p. 218° (decomp.), separates from alcohol in brilliant crystals. The *methiodide*, m. p. 205° (decomp.), crystallises in prisms. The *methylamide* of phenylchlorolactic acid, simultaneously produced, separates from boiling alcohol on addition of ether in needles, m. p. 141°. T. A. H.

Action of a Mixture of Ethyl α-Bromobutyrate and *p*-Tolualdehyde on Zinc. Synthesis of β-Hydroxy-β-tolyl-α ethylpropionic Acid. I. Mazurevitsch (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 183—195. Compare Zeltner, Abstr., 1907, i, 23).—*Ethyl β-hydroxy-β-tolyl-α-ethylpropionate*, $C_6H_4Me{\cdot}CH(OH){\cdot}CHEt{\cdot}CO_2Et$, b.p. 190·5—191°/28 mm., has been prepared by a similar process to that used by Zeltner in the formation of the isomeric α-dimethyl compound, zinc being employed instead of magnesium. The yield can be augmented considerably by using impure aldehyde. On saponifying the ester with potassium hydroxide, the free *acid*, $C_{12}H_{16}O_3$, m. p. 134—135°, is obtained. The *potassium*, *sodium*, *ammonium*, *barium*, *strontium*, *tin*, *zinc*, *mercury*, *nickel*, *iron*, and *aluminium* salts are described. When the acid is heated at its melting point, it decomposes into water, carbon dioxide, and an unsatured hydrocarbon, which is also formed on distillation in steam or when heated with 10% sulphuric acid. Possibly by reactions also occur which produce very small quantities of butyric and *p*-toluic acids. The *hydrocarbon*, $C_6H_4Me{\cdot}CH{:}CHEt$, b. p. 218—218·5°/740 mm., unites with bromine, forming most probably the *dibromide*, $C_{11}H_{14}Br_2$. Z. K.

Piperonylacrylic Acid Dibromide, and its Ethyl Ester. PAUL HOERING (*Ber.*, 1907, 40, 2174—2182).—For the purpose of comparison with *iso*safrole dibromide, the dibromide of piperonylacrylic acid and its ethyl ester were prepared in order to examine what effect the replacement of the terminal methyl group by carboxyl or carbethoxyl groups exerts on the reactivity of the bromine atoms; the effect is intensified.

When ethyl piperonylacrylate is brominated in chloroform solution, the main product is *ethyl piperonylacrylate dibromide*,

$$CH_2O_2{:}C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CO_2Et,$$

which separates in colourless crystals, m. p. 88°. An isomeric dibromide, m. p. 56—57°, is obtained from the mother liquors. The former dibromide was used for the subsequent preparations. When boiled with methyl alcohol, it forms *ethyl β-bromo-α-methoxypiperonylpropionate*, $CH_2O_2{:}C_6H_3{\cdot}CH(OMe){\cdot}CHBr{\cdot}CO_2Et$, which separates from dilute alcohol in colourless needles, m. p. 54—55°; the corresponding *ethoxy*-compound is a colourless oil, and the *hydroxy*-compound,

$$CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHBr{\cdot}CO_2Et,$$

obtained by heating the dibromide with aqueous acetone, separates from light petroleum in prismatic needles, m. p. 62°.

Ethyl β-bromo-α-acetoxypiperonylpropionate,

$$CH_2O_2{:}C_6H_3{\cdot}CH(OAc){\cdot}CHBr{\cdot}CO_2Et,$$

obtained by heating the dibromide with sodium acetate and glacial acetic acid, separates from light petroleum in needles, m. p. 80°.

Ethyl α-ethoxypiperonylacrylate, $CH_2O_2{:}C_6H_3{\cdot}C(OEt){:}CH{\cdot}CO_2Et$, prepared by the action of sodium ethoxide on ethyl β-bromo-α-ethoxypiperonylpropionate, separates from light petroleum in crystals, m. p. 69°. An isomeride separates from the mother liquors in glistening needles, m. p. 55—56°.

Methyl β-bromo-α-methoxypiperonylpropionate,

$$CH_2O_2{:}C_6H_3{\cdot}CH(OMe){\cdot}CHBr{\cdot}CO_2Me,$$

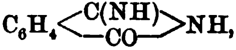
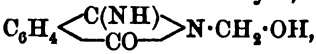
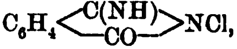
prepared by heating piperonylacrylic dibromide with methyl alcohol, separates from a mixture of alcohol and light petroleum in prisms, m. p. 97—98°.

β-Bromo-α methoxypiperonylpropionic acid separates from a mixture of benzene and light petroleum and has m. p. 150°.

β-Bromo-α-hydroxypiperonylpropionic acid is not formed by the action of aqueous acetone on the dibromide, but a compound, m. p. 228°, which, when dissolved in sodium carbonate and then acidified, gives piperonylacrylic acid.

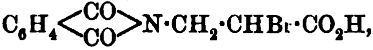
Methylenedioxy-ω-bromostyrene, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CHBr$, is formed by heating piperonylacrylic dibromide with sodium acetate and glacial acetic acid; by the action of bromine it is converted into the *dibromide*, $CH_2O_2{:}C_6H_3{\cdot}CHBr{\cdot}CHBr_2$, which is a yellow oil.

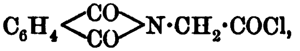
A. McK.

Products of the Action of Acetic Anhydride on Phthalamide. ARSÈNE BRAUN and JOSEPH TSCHERNIAC (*Ber.*, 1907, 40, 2709—2714).—By the action of boiling acetic anhydride on phthalamide, besides acetylphthalamide and phthalonitrile, the chief product formed is *o*-cyanobenzamide, m. p. 172—173°, which then solidifies and melts again above 200°, and is identical with the supposed *o*-cyanobenzaldoxime obtained by Posner (Abstr., 1897, i, 472) from cyanobenzylidene chloride and hydroxylamine. The product formed by heating, or better by the action of alkali hydroxides or ammonia, is *iminophthalimide*,  $C_6H_4{<}\substack{C(NH)\\CO}{>}NH$, which crystallises in hard, colourless crystals, m. p. 203°. With formaldehyde, it forms *hydroxymethyliminophthalimide*,  $C_6H_4{<}\substack{C(NH)\\CO}{>}N\cdot CH_2\cdot OH$, crystallising in colourless clusters, m. p. 143—146° (decomp.), whilst hypochlorites convert it into *iminophthalochloroimide*,  $C_6H_4{<}\substack{C(NH)\\CO}{>}NCl$, crystallising from glacial acetic acid in colourless, glistening needles, m. p. 222—223° (decomp.), which, when heated with alkaline hydroxides, undergoes the Hofmann rearrangement forming *o*-benzoylenecarbamide. Neutral hypochlorite converts *o*-cyanobenzamide into *o*-cyanobenzoic acid, which is not precipitated from its solution in alkali by acetic acid.

E. F. A.

Synthetical Derivatives of Glycine and its Homologues. SIEGMUND GABRIEL (*Ber.*, 1907, 40, 2647—2650).—It is found that phthalimino-derivatives of fatty acids are readily brominated by means of bromine and red phosphorus and these derivatives may be used in a variety of ways for the preparation of *iso*cystein, &c.

a-Bromo-β-phthalylalanine,  $C_6H_4{<}\substack{CO\\CO}{>}N\cdot CH_2\cdot CHBr\cdot CO_2H$, prepared by heating the *β*-phthalylalanine, phosphorus and bromine at the temperature of the water-bath for four to five hours, crystallises from a mixture of water and alcohol in quadratic plates, m. p. 169—170°. On hydrolysis with hydrobromic acid, *a-bromo-β-amino-propionic acid hydrobromide* is obtained.

Phthalylglycyl chloride,  $C_6H_4{<}\substack{CO\\CO}{>}N\cdot CH_2\cdot COCl$, obtained from phthalylglycine and phosphorus pentachloride, crystallises in needles m. p. 84—85°.

W. R.

Phenolphthalein. HANS MEYER (*Ber.*, 1907, 40, 2430—2433).—A criticism of part of Green and King's investigation (Abstr., 1906, i, 670) and also of Meyer and Marx's recent work (this vol., i, 421). The colourless diethoxy- or dimethoxy-lactoid derivatives of tetrabromophenolphthalein are readily obtained by shaking a solution of this compound in excess of potassium hydroxide with the alkyl sulphate.

The *methoxy-lactoid derivative*, $C_{20}H_8O_2Br_4(OMe)_2$, so prepared, forms brilliant, colourless crystals, m. p. 205—206°.

W. H. G.

Dinitrophenylpyridinium Chloride and its Transformation Products. V. Action of Acetic Anhydride on Pyridine Dye Bases. THEODOR ZINCKE and FR. SCHREYER (*Annalen*, 1907, 353, 380—385. Compare Abstr., 1904, i, 448, 921; 1905, i, 467, 923).—It is found now that the acetyl compound, formed together with *p*-chloroacetanilide by the action of acetic anhydride on the base obtained from the di-*p*-chlorodianilide hydrochloride, m. p. 143°, has the constitution $CHO\cdot CH\colon CH\cdot CH\colon CH\cdot NAc\cdot C_6H_4Cl$, and not that ascribed to it previously (Abstr., 1904, i, 923). This aldehyde, m. p. 126°, and not 129° as given (*loc. cit.*), is decomposed readily by alcoholic hydrogen chloride forming *p*-chloroacetanilide, reacts with aniline in alcoholic solution in presence of hydrogen chloride forming the dianilide hydrochloride, $NPh\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot NHPh,HCl$, or with *p*-chloroaniline forming the di-*p*-chlorodianilide hydrochloride, and yields a *phenylhydrazone*,

$$NHPh\cdot N\colon CH\cdot CH\colon CH\cdot CH\colon CH\cdot NAc\cdot C_6H_4Cl,$$

crystallising in yellow leaflets, m. p. 175° (decomp.). When hydrolysed with sodium methoxide in acetone or methyl alcoholic solution, it yields the *aldehyde*, $CHO\cdot CH\colon CH\cdot CH\colon CH\cdot NH\cdot C_6H_4Cl$, which crystallises in yellow leaflets or reddish-yellow needles, m. p. 109° (decomp.). This reacts with aniline forming the dianilide hydrochloride, and yields a *phenylhydrazone*, $N_2HPh\colon C_5H_5\cdot NH\cdot C_6H_4Cl$, crystallising in yellow leaflets, m. p. 119° (decomp.). G. Y.

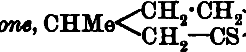
Isomeric Forms of 3-Methyl*cyclo*hexenone. PAUL RABE (*Ber.*, 1907, **40**, 2482—2489. Compare Abstr., 1904, i, 509).—Methyl*cyclo*-Δ^1-hexene-3-one, prepared by the methods given by Hagemann (Abstr., 1893, i, 393) and by the author (*loc. cit.*), mixes in all proportions with water, whilst the product of Knoevenagel's method of preparing this compound (Abstr., 1895, i, 51) is partly miscible with, and partly sparingly soluble in, water. The author finds that methyl*cyclo*-Δ^1-hexene-3-one exists in two isomeric modifications, the one miscible with water being termed the α- and the other the β-form. The investigations carried out with a view to ascertaining the nature of the isomerism have, up to the present, yielded the following results.

[With RICHARD EHRENSTEIN.]—The α- and β-forms have the same molecular weight and both yield γ-acetylbutyric acid on oxidation with alkaline permanganate solution. The molecular refraction is the same in the two cases and agrees with the value calculated for an unsaturated alcohol of the formula $C_7H_9\cdot OH$ containing two double linkings. The two modifications have the same boiling point, sp. gr., and refractive index, and exhibit the same chemical behaviour; the only differences observed lying in (1) the solubility in water and (2) the colour given with ferric chloride solution, the α-compound yielding a faint red coloration, whilst the β-form gives a more intense reddish-violet solution. The *semicarbazone*, $C_8H_{13}ON_3$, prepared from either isomeride, crystallises from dilute alcohol in white needles, m. p. 199°. The action of sodium on ethereal solutions of the two ketones yields the sodium derivatives, both of which give the α-ketone on treatment with sulphuric acid. Similarly, the sodium hydrogen sulphite compounds formed by the two isomerides both yield the α-ketone when boiled with potassium carbonate.

The above observations are insufficient to permit of a definite decision concerning the nature of the isomerism between the α- and β-modifications, but the author suggests that these may consist of allelotropic mixtures of desmotropic forms.

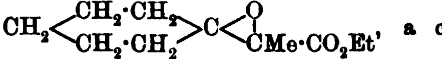
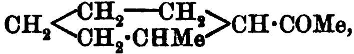
An alcoholic solution of the liquid 1 : 3-dimethy*cyclo*hexene-5-one or of the solid 3-phenyl-1-methyl*cyclo*hexene-5-one gives a violet coloration on addition of ferric chloride, whilst with either of the stereoisomeric 1 : 2 : 3-triphenyl*cyclo*hexene-5-ones only an extremely faint wine-red colour is produced. T. H. P.

Action of Phosphorus Trisulphide on Menthone. NICOLAS A. SPERANSKY (*J. Russ. Phys. Chem. Soc.* 1906, **38**, 1346—1350).—So far, the only thioketones known are such as have the sulphur atom attached to a carbon atom not in the ring, and even these are very few and difficult to obtain. By treating menthone with phosphorus trisulphide the following substances are obtained :

(1) *Thionmenthone*,  $CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2—CS\end{matrix}>CH\cdot CHMe_2$, b. p. 217—220°/760 mm., D^{15}_{15} 0·9398, insoluble in water, but soluble in most organic solvents, decomposes when kept, and with an alcoholic solution of mercury chloride yields small, bright crystals, probably the mercury chloride salt of thiomenthone.

(2) *Thiomenthene*, $C_{20}H_{34}S$, the structural formula of which has not yet been elucidated, forms colourless crystals, m. p. 50·5°, b. p. 213°/28 mm. with slight decomposition.

(3) Menthene, b. p. 168—170°. Other cyclic ketones also yield sulphur derivatives with phosphorus trisulphide. Z. K.

Glycidic Synthesis of Hexahydroaromatic Ketones. GEORGES DARZENS (*Compt. rend.*, 1907, **144**, 1123—1124. Compare Abstr., 1906, i, 430).—*cyclo*Hexanone and its *o*-, *m*-, and *p*-methyl derivatives condense with ethyl *a*-chloropropionate giving good yields of the corresponding trisubstituted glycidic esters according to the general reaction previously described (Abstr., 1906, i, 62). *cyclo*Hexanone gives the *glycidic ester*,  $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}O\\|\\CMe\cdot CO_2Et\end{matrix}$, a colourless, oily liquid with a faint, fruity, rather disagreeable odour, b. p. 154—156°/40 mm. The ester is easily saponified, yielding an acid, which when distilled in a vacuum is decomposed with the formation of Bouveault's hexahydroacetophenone (Abstr., 1904, i, 62). Similarly, *o*-methyl*cyclo*hexanone gives a *glycidic ester*, b. p. 127—129°/15 mm., the acid from which decomposes into carbon dioxide and o-*methylhexahydroacetophenone*,  $CH_2<\begin{matrix}CH_2—CH_2\\CH_2\cdot CHMe\end{matrix}>CH\cdot COMe$, a liquid, b. p. 77—80°/18 mm., which forms a *semicarbazone*, m. p. 172—173°, and combines readily with sodium hydrogen sulphite. *m*-Methyl*cyclo*hexanone gives a *glycidic ester*, b. p. 143—144°/22 mm., of which the corresponding acid forms m-*methylhexahydroacetophenone*, b. p. 99—100°/38 mm. The latter forms a *semicarbazone*, m. p. 174—175°, but does not combine with sodium hydrogen sulphite. The corresponding *ester* from 1-methyl*cyclo*hexane-4-one has b. p. 129—130°/13 mm., and gives a *ketone* having b. p. 75—76°/14 mm. The latter forms a *semicarbazone*, m. p. 158—159°, and combines readily with sodium hydrogen sulphite. Menthone and pulegone do not give glycidic esters when similarly treated. E. H.

Action of Organo-magnesium Compounds on the Alkylidene Cyclic Ketones. HENRI DE BÉVILLE (*Compt. rend.*, 1907, **144**, 1221—1222. Compare Haller and Bauer, Abstr., 1906, i, 441; Kohler, this vol., i, 535).—By the action of magnesium ethyl iodide on active benzylidenemethyl*cyclo*hexane-3-one there are produced (1) a solid, $C_{16}H_{22}O$, in white crystals, m. p. 135°, and (2) a colourless liquid having an agreeable odour, b. p. 160—162°/10 mm; this has not yet been obtained quite pure, but is probably the hydrocarbon $C_{16}H_{20}$. Similar products are obtained when magnesium *n*-propyl iodide is substituted for the ethyl compound. In this case, the solid, $C_{17}H_{24}O$, forms small, white needles, m. p. 84°, whilst the liquid (also slightly impure) has b. p. 180—184°/14 mm, and is probably the hydrocarbon $C_{17}H_{22}$. E. H.

2 : 2′-Dinitrobenzoin. JOAN POPOVICI (*Ber.*, 1907, **40**, 2562—2563).—2 : 2′-*Dinitrobenzoin*, $NO_2\cdot C_6H_4\cdot CO\cdot CH(OH)\cdot C_6H_4\cdot NO_2$, prepared by heating *o*-nitrobenzaldehyde in presence of potassium cyanide, alcohol, and water, crystallises from alcohol in long, pale yellow needles, m. p. 155·5°, and dissolves readily in glacial acetic acid or chloroform.

2 : 2-Dinitrobenzil, prepared by oxidising *o*-dinitrobenzoin by means of chromic acid in acetic acid solution, crystallises from alcohol in colourless rods, m. p. 151°, and is probably identical with the compound, m. p. 147°, described by Zagumenny (this Journal, 1873, 502). T. H. P.

Triketones. IV. FRANZ SACHS and VICTOR HEROLD (*Ber.*, 1907, **40**, 2714—2730).—The method of Ehrlich and Sachs of condensing aromatic nitroso-compounds with "acid" methylene derivatives in presence of an alkaline condensing agent and subsequent hydrolysis with mineral acids whereby the elements of water are taken up in such a way that oxygen replaces the hydrogen atoms of the methylene group, which led to the preparation of triketopentane (Abstr., 1901, i, 670) and of phenyltriketobutane (Abstr., 1902, i, 837), has been extended to other fatty aromatic triketones. Whereas the triketones previously described are reddish-yellow hygroscopic oils, *o*-methoxyphenyl and 2 : 4-dimethoxyphenyltriketobutane are yellow solids.

I. o-*Methoxyphenyltriketobutane.*—Salicylic acid can be directly methylated, with excellent yields, to the dimethyl ester by means of methyl sulphate. This is condensed with acetone under special precautions to *o*-methoxybenzoylacetone, m. p. 37°, of which the iso*nitroso*-derivative, $COMe\cdot C(:N\cdot OH)\cdot CO\cdot C_6H_4\cdot OMe$, forms colourless plates, m. p. 163·5°, whilst the p-*nitrobenzeneazo*-derivative separates in reddish-yellow prisms, m. p. 150°.

When condensed with nitrosodimethylaniline, the ketone forms 4-*dimethylaminophenyl*-o-*methoxybenzoylacetylazomethine*,

$$NMe_2\cdot C_6H_4\cdot N:CAc\cdot CO\cdot C_6H_4\cdot OMe,$$

crystallising in brilliant, red needles, m. p. 125° (sinters at 120°). When hydrolysed with sulphuric acid and extracted with ether, this yields an oil, b. p. 210—225°/25 mm., which solidifies to yellow crystals of o-*methoxyphenyltriketobutane*, $OMe\cdot C_6H_4\cdot CO\cdot CO\cdot COMe$, separating from ethyl acetate in straw-yellow cubes, m. p. 78° (decomp. at 220°). The triketone reduces copper solutions and gives a characteristic dark red ring if the benzene solution containing thiophen be allowed to run on to concentrated sulphuric acid.

It condenses with *o*-phenylenediamine to form 2-*acetyl*-3-o-*methoxyphenylquinoxaline*, separating in colourless needles, m. p. 136—137°, and forming a *phenylhydrazone* identical with that obtained by the action of phenylenediamine on methoxyphenyltriketobutane phenylhydrazone. The *monosemicarbazone* of the triketone forms colourless, matted needles, m. p. 188·5°, and the two remaining *o*-carbonyl groups react with phenylenediamine forming a *compound*, $C_{18}H_{17}O_2N_5$, crystallising in colourless plates, m. p. 247—248° (decomp.). The *monophenylhydrazone* of the triketone crystallises from methyl alcohol in reddish-yellow prisms, m. p. 146·5°, and reacts with phenylenediamine as already mentioned to form a *compound*, $C_{23}H_{20}ON_4$, crystallising in yellow needles, m.p. 131°, which dissolves in concentrated sulphuric acid with a blue coloration.

The triketone forms an additive compound with *p*-nitrophenylacetonitrile, $OMe\cdot C_6H_4\cdot CO\cdot CAc(OH)\cdot CH(CN)\cdot C_6H_4\cdot NO_2$, separating in colourless plates, m. p. 148°; this shows a violet coloration with alkali or ammonia and reduces copper sulphate to copper. Ammonia converts the triketone into *methylsalicylamide*, $OMe\cdot C_6H_4\cdot CO\cdot NH_2$, crystallising in colourless needles, m. p. 125°.

II. 2 : 4-*Dimethoxyphenyltriketobutane*.—The *oxime* of resacetophenone dimethyl ether forms colourless columns aggregated in bunches, m. p. 125°. The dimethyl ether condenses with ethyl acetate to form 2 : 4-*dimethoxybenzoyl acetone*, which separates in colourless, rhombic plates, m. p. 58·5°, and forms an iso*nitroso*-derivative, colourless plates, m. p. 144·5°, and a p-*nitrobenzeneazo*-compound which crystallises in yellowish-brown needles, m. p. 161°. When condensed with nitrosodimethylaniline, the ketone gives rise to 4-*dimethylaminophenylacetyl*-2 : 4-*dimethoxybenzoylazomethine*, which crystallises in splendid ruby-red prisms, m. p. 183°. 2 : 4-*Dimethoxyphenyltriketobutane*,

$$C_6H_3(OMe)_2\cdot CO\cdot CO\cdot COMe,$$

separates in yellow, well-formed, prismatic plates, m. p. 97°, of deeper tone than the monomethoxy-triketone, but otherwise has similar properties; it forms 2-*acetyl*-3-o-p-*dimethoxyphenylquinoxaline*, yellow needles, m. p. 116°; a *monosemicarbazone*, colourless needles, m. p. 191°. It forms no hydrate, but the middle carbonyl can be acetalised and the product yields with *o*-phenylenediamine the *diethylacetal* of 2 : 4-*dimethoxyphenyltriketobutane*-o-*aminophenylimide*, separating in bright yellow plates, m. p. 181°.

III. 2 : 3 : 4-*Triketohexane*.—[With Paul Alsleben.]—Diketohexane was condensed with nitrosodimethylaniline and the azomethine formed immediately hydrolysed to 2 : 3 : 4-*triketohexane*, a mobile, ruby-red oil, b. p. 70°/18 mm., which acts as a powerful reducing agent and, like triketopentane, forms a *hydrate*. It dyes wool and silk yellow, but has no action on cotton. With *o*-phenylenediamine, either 2-*propionyl*-3-*methylquinoxaline* or 2-*acetyl*-3-*ethylquinoxaline* is formed, the product crystallising in bright yellow, rhombic plates, m. p. 56°.

The *bisphenylmethylhydrazone* of triketopentane separates from alcohol in well-formed, yellow rhombs, m. p. 126° (decomp.), whereas the *bisbromophenylhydrazone* forms glistening, brownish-yellow, rhombohedric prisms, m. p. 145° (decomp.). E. F. A.

Phenanthrene Series. XX. Constitution and Colour of Phenanthraquinone Derivatives. JULIUS SCHMIDT and JULIUS SÖLL (*Ber.*, 1907, **40**, 2454—2460).—Notwithstanding the fact that they possess a quinonoid structure, the dibenzoyl and dimethyl derivatives of phenanthraquinonedioxime, likewise the anhydride of the dioxime, have been obtained in a colourless form.

The use of barium carbonate for the liberation of free hydroxylamine from its hydrochloride is recommended in the preparation of phenanthraquinonedioxime and of oximes generally, a quantitative yield being readily obtained. *Phenanthraquinonedioxime dimethyl ether*, $C_{14}H_8(NOMe)_2$, prepared by the interaction of the dioxime with methyl sulphate in the presence of a large excess of sodium hydroxide, crystallises in colourless plates, m. p. 145—146°. At the same time is obtained what appears to be the *monomethyl ether*, $OH\cdot N:C_{14}H_8:N\cdot OMe$, pale yellow needles, m. p. 222—223°. The *dibenzoyl* derivative, $C_{14}H_8(NOBz)_2$, prepared by the Schotten-Baumann method, crystallises in white, silvery leaflets, m. p. 209—210°. The anhydride of the dioxime, $C_{14}H_8ON_2$, described by Goldschmidt (Abstr., 1884, 62) as a yellow substance, crystallises when pure in white needles, m. p. 186—187°. W. H. G.

Two New Terpenes. OSSIAN ASCHAN (*Ber.*, 1907, **40**, 2750—2755).—The mixture of liquid hydrochlorides, obtained on saturating crude American pinene with hydrogen chloride, when decomposed with bases yields a fraction, b. p. 145—148°, of constant rotatory power. This $C_{10}H_{16}$ terpene is termed *pinolene*, and has D_4^{20} 0·8599 $[\alpha]_D$ +1·63, n_D 1·45768. The hydrochloride, $C_{10}H_{17}Cl$, is a paraffin-like substance, m. p. 38°, $[\alpha]_D$ +9·78°. Pinolene takes up a molecule of bromine; it is not attacked by 20% oxalic acid or 10% sulphuric acid, but is oxidised by permanganate, forming as chief product a sparingly soluble, syrupy acid. On heating with a mixture of acetic and 50% sulphuric acids, an *alcohol*, $C_{10}H_{17}\cdot OH$, b. p. 202—203°, is formed, which smells like menthol and fusel oil, and yields a liquid *ketone*, $C_{10}H_{16}O$, b. p. 200°, on oxidation, the *semicarbazone* of which crystallises in large, oblique, glass-glistening plates, m. p. 224—225°.

Pinolene hydrochloride, when heated with aniline and distilled, yields an isomeric hydrocarbon, iso*pinene*, b. p. 154—156°, D_4^{20} 0·8648, $[\alpha]_D^{20}$ +6·0, mol. ref. 43·77, which is thus a dicyclic terpene with a double linking. It decomposes 1 mol. of bromine and forms a glistening, crystalline *hydrochloride*, $C_{10}H_{17}Cl$, m. p. 36—37°, $[\alpha]_D^{22}$ +9·18, which is probably identical with that obtained from pinolene. When heated with acetic and sulphuric acids, *iso*pinene gives rise to an *alcohol*, b. p. 200—203°, and a *ketone*, b. p. 200° (*semicarbazone*, m. p. 221°), possibly identical with those obtained from pinolene. E. F. A.

Essential Oil of the Pacific Arbor Vitæ. WALTER C. BLASDALE (*J. Amer. Chem. Soc.*, 1907, **29**, 539—541).—From 13·8 kilos. of leaves of the Pacific arbor vitæ (*Thuja plicata*), 400 c.c. of a dark brown, volatile oil were obtained, which has a penetrating, terpene-like odour, b. p. 150—225°, D^{15} 0·8997, n_D 1·4575, and a_D 1°45′ (100 mm.). distillation, the largest fraction collected at 198—200° and consisted of thujone (apparently a mixture of the two optically active modifications). The constituents of the other fractions were not identified.

The wood of the plant has a peculiar odour, which is due to the presence of a volatile *substance*, $C_{10}H_{12}O_2$, m. p. 80°, which forms white crystals. E. G.

Barbaloin: its Existence in most Aloes. Composition and Formula. Eugène Léger (*J. Pharm. Chim.*, 1907, **25**, [vi], 513—517. Compare this vol., i, 545).—Although it has now been established that barbaloin occurs in Barbados, Curaçoa, Cape, Socotra, Uganda, and Jafferabad aloes (*Bull. Soc. chim.*, 1902, [iii], **27**, 1902; this vol., i, 545; compare Tschirch and Klaveness, Abstr., 1901, i, 602), there is still a tendency to use specific names for the aloins isolated from various aloes, and there is reason to believe that Aschan's "feroxaloin" (Abstr., 1903, i, 772) is merely barbaloin, although the identity of zanaloin and barbaloin is still doubtful (compare Tschirch and Hoffbauer, Abstr., 1905, i, 913). The various formulæ proposed for barbaloin, $C_{17}H_{18}O_7$ (Stenhouse), $C_{15}H_{16}O_7$ (Liebelt), $C_{16}H_{18}O_7$ (Tilden), $C_{17}H_{20}O_7$ (Treumann), $C_{16}H_{16}O_7$ (Grœnwold), are incompatible with the production from this substance, by the action of sodium peroxide or by the prolonged action of alcohol, of *iso*hydroxymethylchrysasin and aloinose (methyl aldopentose), and, further, it is difficult to account for the optical activity of barbaloin by means of such formulæ. The ebullioscopic measurements made by Tschirch and Klaveness (*loc. cit.*) do not afford satisfactory evidence in favour of Grœnwold's formula, as the changes in temperature obtained were small and variable, and this also applies to Aschan's observations (Abstr., 1903, i, 772). The formula proposed by the author, $C_{21}H_{20}O_9$ (Abstr., 1902, i, 685; 1903, i, 356; 1904, i, 907), is, on the contrary, in accordance with the analytical data, cryoscopic measurements of the mol. weight of the chloroacetyl derivative, and the hydrolytic products of barbaloin. T. A. H.

A New Crystalline Substance from Fresh Kola. Goris (*Compt. rend.*, 1907, **144**, 1162—1164).—Kola nuts, sterilised by heating at 105° in an autoclave for ten minutes, are powdered and extracted with hot 80% alcohol, or better, lixiviated with cold alcohol. The alcoholic extract, when evaporated in a vacuum, gives a syrup which, after repeated washing with chloroform, gradually crystallises. The white crystals so obtained seem to be a loose combination of caffeine and a substance, *kolatin*, probably belonging to the group of tannins. The caffeine is removed by dissolving the crystals in water and extracting with chloroform. Kolatin is a phenolic compound, $C_8H_{10}O_4$, crystallising in prismatic needles, which under certain conditions oxidise to a red, insoluble powder and, similarly to sodium benzoate and salicylate, dissolve caffeine. Dried Kola nuts and their pharmaceutical extract do not contain kolatin, which disappears during drying. The sterilised nuts yield 15 grams of the kolatin-caffeine substance, or about half as much kolatin per kilogram. E. H.

Synthesis of Unsymmetrical Substituted Thianthrenes. JAROSLAV FRÖHLICH (*Ber.*, 1907, **40**, 2489—2492. Compare Hillyer, Abstr., 1902, i, 50; Mauthner, Abstr., 1905, i, 461).—By the action of picryl chloride on 2-amino-1-methylphenylene-4 : 5-dithiol (Fröhlich and Fichter, *Verh. Naturf. Ges. Basel*, **19**, 44), an unsymmetrical dinitromethylaminothianthrene (compare Krafft and Kaschau, Abstr., 1896, i, 297) is obtained.

1 : 3-*Dinitro*-7-*amino*-6-*methylthianthrene* (? 1 : 3-*dinitro*-6-*amino*-7-*methylthianthrene*), $C_{13}H_9O_4N_3S_2$, crystallises from alcohol in red, coppery leaflets, m. p. 203°, and forms a diazo-derivative which yields a poppy-red dye with β-naphthol.

1 : 3 : 7-*Triamino*-6-*methylthianthrene* (? 1 : 3 : 6-*triamino*-7-*methylthianthrene*), $C_{13}H_{13}N_3S_2$, obtained by reducing the preceding compound, yields a *hydrochloride*, $C_{13}H_{13}N_3S_2,3HCl$, crystallising in white needles.

1 : 3-*Dinitro*-7-*diacetylamino*-6-*methylthianthrene* (? 1 : 3-*dinitro*-6-*diacetylamino*-7-*methylthianthrene*), $C_{17}H_{13}O_6N_3S_2$, prepared by acetylating the dinitroamino-compound, separates from a mixture of benzene and light petroleum in microscopic, yellow crystals, m. p. 168°.

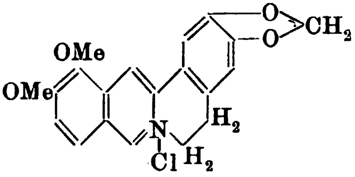
2-*Diacetylamino*-1-*methylphenylene*-4 : 5-*dithiolacetate*,

$$NAc_2\cdot C_6H_2Me(SAc)_2,$$

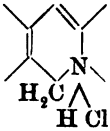
prepared by acetylating 2-amino-1-methylphenylene-4 : 5-dithiol, crystallises from alcohol in pale brown plates, m. p. 112°.

T. H. P.

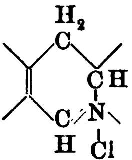
Homologues of Berberine and Canadine. MARTIN FREUND and FRITZ MAYER (*Ber.*, 1907, **40**, 2604—2614).—If Gadamer's modification (compare Abstr., 1902, i, 555) of Perkin's formula for berberine (compare Trans., 1894, **65**, 63; 1895, **67**, 991) be accepted, the conversion of the hydrochloride (I) into *r*-canadine by the addition of four atoms of hydrogen should take place in two steps. The addition of the first pair of hydrogen atoms may occur as in (II), followed by elimination of hydrogen chloride, or as in (III). The former compound has been obtained by Gadamer (*Chem. Zeit.*, **26**, 385) and its homologues by Freund and Beck (Abstr., 1905, i, 151). These homologues of dihydroberberine contain one asymmetric carbon atom; by the addition of a second pair of hydrogen atoms, another carbon atom becomes asymmetric as in (IV), and consequently two



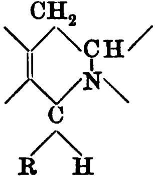
(I.)



(II.)



(III.)



(IV.)

stereoisomeric racemic tetrahydro-bases ought to exist, a deduction which has been realised in the case of propyltetrahydroberberine, although neither of the racemic bases has as yet been resolved into its active constituents.

By the removal of two atoms of hydrogen from the alkyldihydroberberines, the corresponding homologues of berberine have been obtained in the form of salts, but the free bases have not been prepared in a pure state.

a-*Methyltetrahydroberberine hydrochloride*, $C_{21}H_{23}O_4N,HCl$, m. p. 264°, crystallises in white needles, and is obtained by the addition of dilute hydrochloric acid to an alcoholic solution of a-methyltetrahydroberberine (Abstr., 1905, i, 657).

a-*Methylberberine hydriodide*, $C_{21}H_{19}O_4N,HI$, forms golden-yellow needles, decomposes at 255—260°, and is most conveniently prepared by treating a-methyldihydroberberine hydriodide with bromine in hot glacial acetic acid and digesting the dark brown mass which separates with sulphurous acid. The *nitrate*, $C_{21}H_{19}O_4N,HNO_3$, forms yellow needles and decomposes at 240—260°.

a-*Ethyldihydroberberine*, $C_{22}H_{23}O_4N$, m. p. 164—165°, is obtained in the form of the *hydriodide*, m. p. 223°, in a similar manner to the methyl compound (compare Freund and Beck, *loc. cit.*).

a-*Ethyltetrahydroberberine*, $C_{22}H_{25}O_4N$, m. p. 151—152°, is obtained in a similar manner to the methyl compound by the electrolytic reduction of a-ethyldihydroberberine (Abstr., 1905, i, 657); the *hydrochloride*, $C_{22}H_{25}O_4N,HCl$, crystallises in white leaflets, softens at 220°, and has m. p. 245° (decomp.).

a-*Ethylberberine hydriodide*, $C_{22}H_{21}O_4N,HI$, obtained in a similar manner to the methyl homologue, separates from dilute alcohol in slender, yellow needles, darkens at 230°, and decomposes at 248°; the *nitrate* decomposes at 240°.

a-*Propyldihydroberberine*, $C_{23}H_{25}O_4N$, m. p. 132°, forms yellow leaflets; its *hydriodide* has m. p. 207°. The electrolytic reduction of the base leads to the formation of a basic mixture which, after conversion into the nitrates, is treated with a quantity of hot alcohol insufficient for complete solution. The filtrate contains *a-propyltetrahydroberberine nitrate*, m. p. 203—212° (decomp.), which forms white needles and is soluble in hot dilute alcohol; the free *base*, $C_{23}H_{27}O_4N$, m. p. 111—114°, crystallises in flat prisms, and exhibits a faint greenish-yellow fluorescence; the *hydrochloride* has m. p. 230—240° (decomp.). From the residual nitrate which has not dissolved in the alcohol, *ψ-a-propyltetrahydroberberine*, m. p. 177—179°, is obtained; it crystallises in flat plates, and forms a *nitrate*, m. p. 200° (decomp.), and a *hydrochloride*, m. p. 245° (decomp.), which are sparingly soluble in hot aqueous alcohol.

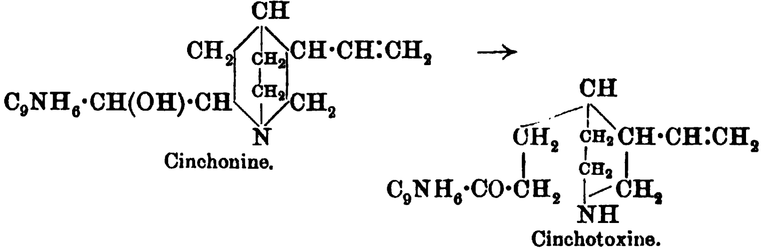
a-*Propylberberine hydriodide*, $C_{23}H_{23}O_4N,HI$, m. p. 246° (decomp.), forms golden-yellow needles, and is prepared in a similar manner to the methyl homologue.

The physiological action of a-methyltetrahydroberberine hydrochloride is very slight; ethyldihydroberberine hydrochloride has a pronounced local effect. C. S.

Carnosine. Friedrich Kutscher (*Zeitsch. physiol. Chem.*, 1907, 51, 545—548).—Polemical against Gulewitsch (compare this vol., i, 436). W. D. H.

Quinine Alkaloids. Georg Rohde and A. Antonaz (*Ber.*, 1907, 40, 2329—2338).—In the preparation of *iso*nitrosomethylquinotoxine (Abstr., 1905, i, 228) by the action of sodium ethoxide and amyl nitrite on methylquinotoxine, a 10% yield of a by-product is obtained in the form of yellow, glistening needles. These consist of a sodium derivative which is not decomposed by carbon dioxide, and from which dilute mineral acids precipitate quinic acid. The formation of this acid is quantitative when a solution of methylquinotoxine in absolute alcohol is mixed with the requisite amount of sodium ethoxide and nitrobenzene (2 mols.) and kept overnight. Quinotoxine behaves in a similar manner, and cinchotoxine yields cinchoninic acid. The other decomposition product may be meroquinine, but so far all attempts to identify and isolate it have proved fruitless. Small amounts of aniline and of azoxybenzene have been isolated from the mixtures. Nitrosoquinotoxine and the sulphonamide of cinchotoxine are not decomposed by sodium ethoxide and nitrobenzene. The *sulphonamide*, $C_{25}H_{26}O_3N_2S$, is crystalline, has m. p. 108—109°, and is only sparingly soluble in cold alcohol or ether.

The fact that *iso*nitrosomethylquinotoxine is not decomposed by the same method indicates that the carbinol group of the toxine bases (compare Rabe and Ritter, this vol., i, 78; Koenigs, this vol., i, 345) is adjacent to a carbon atom of the quinoline ring. It is suggested that cinchonine is not a tertiary but a secondary alcohol:



Cinchonine.

Cinchotoxine.

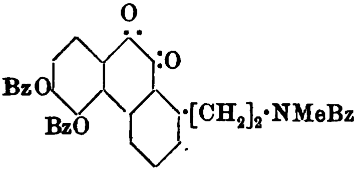
J. J. S.

Solubility of Morphine in Ethyl Ether. M. Marchioneschi (*Boll. Chim. Farm.*, 1907, 46, 389—391).—The amount of morphine remaining in solution after heating the alkaloid with boiling ether during two hours and allowing the solution to cool at 5·5° during forty-eight hours was determined. The solubility under such conditions is greatest for anhydrous morphine in dry ether distilled from sodium, being 0·56 gram per litre. In the case of crystalline morphine ($C_{17}H_{19}O_3N,H_2O$) and dry ether distilled from sodium, the solubility is 0·23 gram per litre, whilst for the same substance in ordinary ether previously washed with aqueous sodium hydroxide and distilled it is about 0·05 gram per litre. W. A. D.

Constitution of *apo*Morphine. Constitution of Morphine. Robert Pschorr (*Ber.*, 1907, **40**, 1984—1995. Compare Abstr., 1903, i, 193).—*apo*Morphine contains two phenolic hydroxyl groups and as morphine contains only one of these groups, the formation of *apo*morphine from morphine by concentrated hydrochloric acid must involve the conversion of the "ether-like" oxygen of the morphine into the second phenolic hydroxyl grouping. To further prove the constitution of *apo*morphine, tribenzoyl*apo*morphine (*loc. cit.*) was oxidised to a phenanthraquinone derivative containing all the original substituents (compare following abstract). This result excludes therefore the possibility of substitution having occurred in the medial ring of the phenanthrene nucleus. The 3 : 4-dimethoxyphenanthrenecarboxylic acid was converted into 3 : 4 : 8-trimethoxyphenanthrene by Curtius' method and this establishes the position of the carboxyl group; consequently the carbon chain of the side-ring must be united to position-8 of the phenanthrene nucleus. These considerations support the constitution formerly ascribed to *apo*morphine (*loc. cit.*).

W. R.

Oxidation of Tribenzoyl*apo*morphine. Robert Pschorr and O. Spangenberg (*Ber.*, 1907, **40**, 1995—1998).—*Tribenzoyl*apo*morphinequinone* (annexed formula), obtained by the action of chromic acid on an acetic acid solution of tribenzoyl*apo*morphine, crystallises in yellowish-red rods from ethyl acetate; m. p. 178—179° (corr.). It gives the same colour reactions as diacetylmorphol. The *phenylhydrazone*, $C_{44}H_{33}O_6N_3$, crystallises in glistening, red leaflets, m. p. 235—236° (corr.). The *azine* from *o*-phenylenediamine, $C_{44}H_{31}O_5N_3$, forms light yellow needles, m. p. 221—222° (corr.). On hydrolysis with sodium ethoxide, N-*benzoyl*apo*morphinequinone*, $C_{24}H_{19}O_5N$, is formed in red flakes, m. p. 218° (corr.); its *phenylhydrazone* has m. p. 228° (corr.).

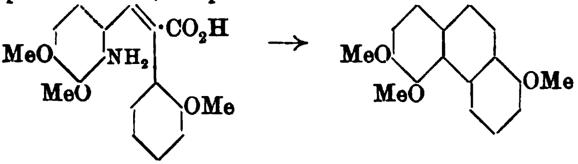


W. R.

Transformation of *apo*Morphine into 3 : 4 : 8-Trimethoxyphenanthrene. Robert Pschorr, Hans Einbeck, and O. Spangenberg (*Ber.*, 1907, **40**, 1998—2001. Compare Abstr., 1906, i, 878; 1903, i, 193).—*Ethyl* 3 : 4-*dimethoxyphenanthrene*-9-*carboxylate*, $C_{19}H_{18}O_4$, forms yellow crystals, m. p. 81—83°, and on treatment with hydrazine hydrate at 100° for twenty hours yields the *hydrazide*, $C_{17}H_{16}O_3N_2$, crystallising in needles, m. p. 194—195°. This was converted into the *urethane*, $C_{19}H_{19}O_4N$, by means of amyl nitrite and hydrogen chloride in alcohol; it crystallises in glistening needles, m. p. 165°. On hydrolysis with alcoholic ammonia at 180° and subsequent acidification, 8-*amino*-3 : 4-*dimethoxyphenanthrene hydrochloride* is obtained in long needles, m. p. 290°. This, by diazotisation, is converted into 3 : 4-*dimethoxy*-8-*phenanthrol*, crystallising in prisms, m. p. 182—183°; by methylation, 3 : 4 : 8-*trimethoxyphenanthrene*, $C_{17}H_{16}O_3$, is obtained. The *picrate* has m. p. 129°.

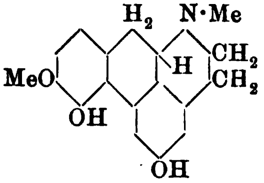
W. R.

Synthesis of 3 : 4 : 8-Trimethoxyphenanthrene. ROBERT PSCHORR and HANS BUSCH (*Ber.*, 1907, 40, 2001—2003).—This communication describes the preparation of trimethoxyphenanthrene, identical in all respects with that obtained from *apo*morphine. Sodium *o*-methoxyphenylacetate on being heated at 120° with 1·5 mol. of *vic.*-*o*-nitrovanillin methyl ether, and acetic anhydride for forty-eight hours, yields *a-o-methoxyphenyl-2-nitro-3 : 4-dimethoxycinnamic acid*, $C_{18}H_{17}O_7N$, crystallising in prisms, m. p. 219—221° (corr.). This, on reduction with ammonia in the presence of ferrous sulphate, gives the corresponding *amino*-acid, $C_{18}H_{19}O_5N$, which forms yellow rhombohedra, m. p. 189—190° (corr.). The conversion into 3 : 4 : 8-trimethoxyphenanthrene-9-carboxylic acid, m. p. 250° (corr.), was accomplished by treatment of the diazo-compound from the amino-acid with copper powder, and this acid when heated with glacial acetic acid at 220—230° loses carbon dioxide and gives 3 : 4 : 8-trimethoxyphenanthrene, m. p. 138° :



W. R.

Constitution of Morphothebaine. ROBERT PSCHORR and W. L. HALLE (*Ber.*, 1907, 40, 2004—2006).—The similarity in properties as well as in its mode of preparation renders it probable that *apo*morphine and morphothebaine are allied in constitution. Tribenzoylmorphothebaine, m. p. 184° (corr.), when oxidised with chromic acid in acetic acid, yields a thick brown oil containing *tribenzoylmorphothebainequinone*, but from which the quinone could not be obtained in a crystalline form. It, however, forms with phenylhydrazine the *tribenzoylmorphothebainequinone phenylhydrazone*, $C_{45}H_{35}O_7N_3$, m. p. 227° (corr.), crystallising in red needles ; with *o*-phenylenediamine it gives the *azine*, $C_{45}H_{33}O_6N_3$, of m. p. 201° (corr.), and crystallising in yellow prisms. N-*Benzoylmorphothebainequinone*, $C_{25}H_{21}O_6N$, is obtained from the uncrystallisable oil by hydrolysis with sodium ethoxide and forms light brown prisms, m. p. 267° (corr.). The *phenylhydrazone*, $C_{31}H_{27}O_5N_3$, forms reddish-brown needles, m. p. 271° (corr.), and the *azine*, $C_{31}H_{25}O_4N_3$, light brown prisms, m. p. 274—275°. Morphothebaine has therefore the annexed constitution.



W. R.

Catalytic Actions of Finely-divided Metals on Nitrogen Compounds. MAURICE PADOA (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 818—822).—In continuation of work previously published (Abstr., 1906, i, 530, 765), the author has investigated the action of reduced nickel, in presence of hydrogen, on pyridine and piperidine.

When pyridine vapour and hydrogen are passed over reduced nickel heated at 180—250°, the products obtained are traces of secondary bases (? piperidine) and a non-basic compound, which has the properties of the pyrroles, but could not be identified owing to the smallness of the yield.

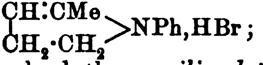
Since piperidine contains sufficient hydrogen to bring about the desired transformation, this compound was submitted to the action of reduced nickel alone, the temperatures employed varying between 180° and 250°. The products obtained consist of: (1) pyridine; (2) pyrrole compounds in larger proportion than in the case of pyridine, but still insufficient for identification; (3) a secondary *base*, $C_{10}H_{21}N$ or $C_5NH_{10}\cdot C_5H_{11}$, b. p. 170—190°, which is obtained as a colourless oil having an odour like that of piperidine, gives Liebermann's reaction for nitroso-compounds, and yields a yellow, crystalline *picrate*,

$$C_{10}H_{21}N,C_6H_3O_7N_3,$$

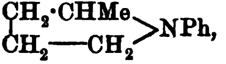
m. p. 125°; (4) a dense, oily *base*, $C_{14}H_{28}N_2$ or $C_5NH_{10}\cdot[CH_2]_4\cdot C_5NH_{10}$, b. p. 175—180°/28 mm., which yields a *picrate*, $C_{14}H_{28}N_2,2C_6H_3O_7N_3$, m. p. 192—193°, an *aurichloride*, m. p. 176—177°, and a *platinichloride*, m. p. 230° (decomp.); the base gives Liebermann's reaction, and has the normal molecular weight in freezing benzene. The constitution and characters of this base are similar to those of α-δ-dipiperidylbutane (Töhl, Abstr., 1895, i, 681). T. H. P.

Action of Aniline and *p*-Toluidine on Methyl γ-Bromopropyl Ketone. Synthesis of *N*-Phenylated Pyrroline and Pyrrolidine Derivatives.

Joseph Markwalder (*J. pr. Chem.*, 1907, [ii], 75, 329—368).—It was shown by Lipp (Abstr., 1887, 277) that methyl γ-bromopropyl ketone reacts with ammonia forming a pyrrole derivative, whilst Hielscher (Abstr., 1898, i, 338) found that derivatives of dihydropyrrole are formed by the action of ammonia and of methylamine on the bromo-ketone. The present work was undertaken to determine if this bromo-ketone reacts in the same manner with primary aromatic amines, since tetrahydropyridines are formed by the action of ammonia, or of primary aliphatic or aromatic amines on methyl δ-bromobutyl ketone (Lipp, Abstr., 1892, 1243; 1896, i, 317); to compare the behaviour of the resulting *N*-phenylated dihydropyrroles with that of the corresponding *N*-phenylated tetrahydropyridines, and, in view of the interest attached to the 2-substituted pyrrolidines in their relation to hygrine and the alkaloids of the tropine group (Willstätter, Abstr., 1900, i, 405), to study the products obtained on reduction of the dihydropyrroles in question.

Methyl γ-anilinopropyl ketone, $NHPh\cdot CH_2\cdot CH_2\cdot COMe$, the primary product of the action of aniline on methyl γ-bromopropyl ketone, undergoes immediate condensation in the presence of the hydrogen bromide simultaneously formed, hence the product obtained is 1-*phenyl-2-methyl-4:5-dihydropyrrole hydrobromide*,  $\left.\begin{matrix}CH{:}CMe\\ |\\ CH_2\cdot CH_2\end{matrix}\right>NPh,HBr$; on liberation of the base, the pyrrole ring is resolved, the *γ-anilino-ketone* being formed (compare Freund, Abstr., 1893, i, 116). Whilst reduction of the anilino-ketone with sodium in alcoholic solution leads to the formation of the corresponding *sec.-alcohol*,

$$OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHPh,$$

the reduction by means of tin and hydrochloric acid leads to that of 1-phenyl-2-methylpyrrolidine,  $\begin{matrix}CH_2\cdot CHMe\\ \vert\qquad\qquad\\ CH_2 — CH_2\end{matrix}>NPh$, which is stable on liberation from its salts.

Similar compounds are obtained by the action of *p*-toluidine on methyl γ-bromopropyl ketone.

As Fischer has shown that pyrrolidine-2-carboxylic acid is formed by the hydrolysis of egg-albumin (Abstr., 1901, i, 745), some interest was attached to the oxidation of 1-phenyl-2-methylpyrrolidine to 1-phenylpyrrolidine-2-carboxylic acid; an attempt to accomplish this by means of potassium permanganate and sulphuric acid was unsuccessful.

1-*Phenyl-2-methyl-*4 : 5-*dihydropyrrole hydrobromide* is formed with development of heat by the action of aniline on methyl γ-bromopropyl ketone; the *hydrochloride*, formed by the action of hydrochloric acid on methyl γ-anilinopropyl ketone, and the *sulphate* are obtained as light brown, viscid oils; the *picrate*, $C_{17}H_{16}O_7N_4$, crystallises in yellow needles, m. p. 132°; the orange, crystalline *platinichloride* is unstable.

Methyl γ-*anilinopropyl ketone* crystallises in microscopic leaflets, m. p. 23—25°, and when heated yields an oily *anhydride*, $C_{22}H_{28}ON_2$. The *oxime* of the anilino-ketone, $C_{11}H_{16}ON_2$, crystallises in leaflets, m. p. 86—88^c; the *phenylhydrazone* gives a dark red, almost violet, coloration with ferric chloride in concentrated sulphuric acid solution; the *semicarbazone*, $C_{12}H_{18}ON_4$, forms colourless leaflets, m. p., 142°; the *benzoyl* derivative was obtained as a viscid, light brown oil.

1-Phenyl-2-methylpyrrolidine (Schultz and Friemehlt, Abstr., 1899, i, 541), b. p., 127·5°/13 mm.; the *stannochloride*, m. p., 107—109; the platinichloride, m. p. 114° (decomp.); the picrate, m. p. 110°.

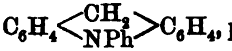
Methyl-γ-*anilinopropylcarbinol* is obtained as a viscid, brown oil, forms syrupy *salts*, and readily loses water; the *benzoyl* derivative is a light brown oil.

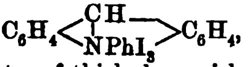
Methyl γ-p-*toluidinopropyl ketone*, $C_{12}H_{17}ON$, formed by the action of *p*-toluidine on methylγ-bromopropyl ketone and treatment of the product with potassium hydroxide, crystallises in needles, m. p. 73° (decomp.); the *oxime hydrochloride* forms needles, m. p. 154°; the *oxime* crystallises in needles or rhombic plates, m. p. 131—132°, and reduces ammoniacal silver and Fehling's solutions when heated.

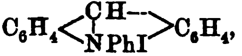
1-p-*Tolyl-2-methyl-*4 : 5-*dihydropyrrole hydrochloride* and *hydrobromide* are deliquescent; the *picrate*, $C_5H_8N\cdot C_7H_7,C_6H_3O_7N_3$, crystallises in scales, m. p. 132°.

Methyl-γ-p-*toluidinopropylcarbinol*, $C_{12}H_{19}ON$, formed by reduction of the ketone with sodium in alcoholic solution, crystallises in slightly brown leaflets, m. p. 64°; the *salts* and *benzoyl* derivative cannot be crystallised. G. Y.

10-Phenylacridinium Compounds. FRITZ ULLMANN and RUDOLF MAAG (*Ber.*, 1907, 40, 2515—2524).—Reduction of 10-phenylacridone by means of sodium and ethyl or amyl alcohol gives a good yield of 10-phenyldihydroacridine, which, on oxidation with iodine, is converted into 10-phenylacridinium periodide. 10-Phenylacridone may also be transformed into compounds of the acridinium series by the action of Grignard's reagent; thus, when magnesium phenyl bromide is used, 9 : 10-diphenylacridol is obtained, the reaction being analogous to that observed by Bünzly and Decker (Abstr., 1904, i, 344) in the case of methylacridone. Of the salts of the new acridinium compounds, the chlorides especially are readily soluble in water giving yellow solutions. When ammonia-solution is added to a solution of the diphenylacridinium chloride, the liquid becomes turbid after some time; the reaction which takes place is analogous to that occurring with the alkyl halogen derivatives of the acridine series investigated by Hantzsch and Kalb (Abstr., 1900, i, 113) and by Decker (Abstr., 1902, i, 691), the first product being an ammonium base, which becomes rapidly transformed into the insoluble acridol. 9 : 10-Diphenylacridol is very stable and yields the corresponding ether on boiling with alcohol. The analogous 10-phenylacridol could not be obtained pure, as it readily undergoes oxidation to 10-phenylacridone.

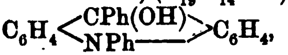
10-*Phenyldihydroacridine*,  $C_6H_4<\begin{matrix}CH_2\\NPh\end{matrix}>C_6H_4$, prepared by the action of sodium on an amyl alcoholic solution of 10-phenylacridone, crystallises from glacial acetic acid in colourless needles or prisms, m. p. 119°.

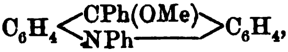
10-*Phenylacridinium periodide*,  $C_6H_4<\begin{matrix}CH-\\|\\NPhI_3\end{matrix}>C_6H_4$, crystallises from alcohol in feather-like aggregates of thick, brownish-red needles.

10-*Phenylacridinium iodide*,  $C_6H_4<\begin{matrix}CH-\\|\\NPhI\end{matrix}>C_6H_4$, prepared by the action of dilute sulphuric acid on the periodide, separates in long, cinnabar-red needles, m. p. 233° (decomp.).

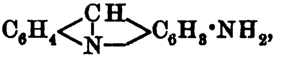
On treating 10-phenylacridinium iodide with benzene and dilute sodium hydroxide solution and passing hydrogen chloride into the dried benzene solution of the 10-phenylacridol thus obtained, 10-*phenylacridinium chloride* separates in oily drops changing to star-shaped aggregates of needles; the yellow alcoholic solution of 10-phenylacridinium chloride, which exhibits an intense green fluorescence, is decolorised by ammonia and then shows a blue fluorescence. 10-Phenylacridinium chloride may also be obtained by passing chlorine into a benzene solution of 10-phenyldihydroacridine.

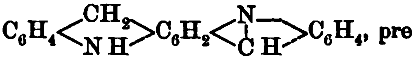
10-Phenylacridinium chloride forms double salts with *ferric chloride*, $C_{19}H_{14}NCl,FeCl_3$, and *platinum chloride*, $(C_{19}H_{14}NCl)_2,PtCl_4$.

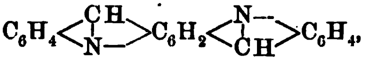
5 : 10-*Diphenylacridol*,  $C_6H_4<\begin{matrix}CPh(OH)\\NPh\end{matrix}>C_6H_4$, crystallises from light petroleum in colourless, glassy prisms, m. p. 178°. The addition of potassium iodide to its solution in dilute acetic acid gives the *iodide*, $C_{25}H_{18}NI$, which crystallises in purple needles. 5 : 10-Diphenylacridol forms a *platinichloride*, $(C_{25}H_{18}NCl)_2PtCl_4$, which separates in yellow needles.

The *methyl ether* of 5 : 10-diphenylacridol,  $C_6H_4<\begin{matrix}CPh(OMe)\\NPh\end{matrix}>C_6H_4$, separates from methyl alcohol in shining, colourless crystals, m. p. 184°.

The conversion of acridone into dihydroacridine is also easily accomplished by reduction with sodium in either ethyl or amyl alcohol.

4-*Aminoacridine*,  $C_6H_4<\overset{CH}{\underset{N}{|}}>C_6H_3\cdot NH_2$, prepared by reducing 1-aminoacridone with sodium in amyl alcohol, separates in yellowish-brown needles.

Dihydroquinacridine,  $C_6H_4<\overset{CH_2}{\underset{NH}{}}>C_6H_2<\overset{N-}{\underset{CH}{|}}>C_6H_4$, prepared by reducing an alcoholic solution of quinacridone (compare Ullmann and Maag, Abstr., 1906, i, 459) by means of sodium or, in small quantity, by distilling quinacridone with zinc dust, crystallises from alcohol in red needles, m. p. 243°; its *hydrochloride*, $C_{20}H_{14}N_2,HCl$, separates in steel-blue crystals.

Quinacridine,  $C_6H_4<\overset{CH}{\underset{N}{|}}>C_6H_2<\overset{N-}{\underset{CH}{|}}>C_6H_4$, prepared by the action of glacial acetic acid and a little nitric acid on dihydroquinacridine, crystallises from alcohol in slender, faintly yellow needles, m. p. 245°. T. H. P.

Condensation of Oxalic Esters with *tert.*-Aromatic Amines. ALFRED GUYOT (*Compt. rend.*, 1907, **144**, 1051–1053. Compare Haller and Guyot, this vol., i, 565).—The oxalic esters react with *tert.*-aromatic amines in presence of a small quantity of aluminium chloride at low temperatures forming dialkylaminophenylglyoxalic esters of the type $NR'_2\cdot C_6H_4\cdot CO\cdot CO_2R$. At higher temperatures or in the presence of more aluminium chloride, the principal products are tetra-alkyldiaminophenylglycollic esters of the type $OH\cdot C(C_6H_4\cdot NR'_2)_2\cdot CO_2R$. At still higher temperatures and in presence of a large excess of aluminium chloride, the substituted glycollic esters are replaced by hexa-alkyltriaminotriphenylacetic esters, $CO_2R\cdot C(C_6H_4\cdot NR'_2)_3$.

All these products are obtained in yields of 50—75% of the theoretical, except in the case of methyl oxalate. The three types of products formed, when treated with sulphuric acid, decompose quantitatively, evolving carbon monoxide, and giving respectively dialkylaminobenzoic acids, $NR'_2\cdot C_6H_4\cdot CO_2H$, tetra-alkyldiaminobenzophenones,

$$CO(C_6H_4\cdot NR'_2)_2,$$

and hexa-alkyltriaminotriphenylcarbinols, $OH\cdot C(C_6H_4\cdot NR'_2)_3$.

Apart from its industrial interest as affording a means of preparing dyes, at present made by the use of carbonyl chloride, this reaction affords an explanation of the formation of such substances as rosolic and pararosolic acids and diphenylamine-blue, since it may be assumed that in the ordinary methods of preparing these substances reactions similar to those described take place, the intermediate products formed being under the conditions of the reaction decomposed with the evolution of carbon monoxide and carbon dioxide giving rise to the dyes. T. A. H.

Products of Condensation of Ethyl Oxalate with Dimethylaniline in Presence of Aluminium Chloride. ALFRED GUYOT (*Compt. rend.*, 1907, **144**, 1120—1123. Compare preceding abstract). —When a solution of ethyl oxalate and dimethylaniline in anhydrous ether is added to a solution of aluminium chloride in dry ether, a 60% (of theory) yield of Michler and Hanhardt's ethyl *p*-dimethylanilinoglyoxylate, $NMe_2 \cdot C_6H_4 \cdot CO \cdot CO_2Et$ (Abstr., 1878, 421), is obtained together with a small quantity of *ethyl tetramethyldiaminodiphenylglycollate*, $OH \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot CO_2Et$. The latter compound becomes almost the sole product if the amount of dimethylaniline is increased, and the ethereal solution of aluminium chloride more dilute.

Ethyl tetramethyldiaminodiphenylglycollate forms transparent, colourless prisms, m. p. 112°, which in the light very rapidly become yellow. It dissolves in acetic acid with an intense indigo-blue coloration, and condenses with tertiary aromatic amines in neutral or acid aqueous solution giving triphenylmethane derivatives,

$$NR_2 \cdot C_6H_4 \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot CO_2Et.$$

It dissolves in concentrated sulphuric acid with an intense yellow colour, and the solution when heated at 140° evolves carbon monoxide and gives a quantitative yield of tetramethyldiaminobenzophenone. If a solution of aluminium chloride in anhydrous ether be rapidly added to a mixture of ethyl oxalate and dimethylaniline, the chief product is *ethyl hexamethyltriaminotriphenylacetate*,

$$C(C_6H_4 \cdot NMe_2)_3 \cdot CO_2Et.$$

It forms colourless crystals, m. p. 176°, and dissolves without coloration in concentrated sulphuric; the solution on heating at 140° suddenly becomes orange-yellow, evolves carbon monoxide, and gives an almost theoretical yield of crystal-violet. Ethyl hexamethyltriaminotriphenylacetate is also formed by the condensation of the above glyoxylate or glycollate or of ethyl aminotetramethyldiaminodiphenylacetate with dimethylaniline, and together with ethyl dimethylanilinoglyoxylate, by the action of ethyl oxalylchloride on dimethylaniline, but not by the action of this base on ethyl trichloroacetate. E. H.

Synthesis of the Auramines by Means of the Oxalic Esters.

ALFRED GUYOT (*Compt. rend.*, 1907, **144**, 1219—1220).—The indigo-blue aqueous solutions of the neutral salts of the tetra-alkyldiaminodiphenylglycollic esters (preceding abstracts) with acids, when treated with ammonia, give, not the corresponding hydroxy-compound, but a tetra-alkyldiaminodiphenylaminoacetic ester, thus:

$$C(C_6H_4 \cdot NR_2)_2Cl \cdot CO_2R' + 2NH_3 = NH_4Cl + NH_2 \cdot C(C_6H_4 \cdot NR_2)_2 \cdot CO_2R'.$$

The new compounds are leucoauraminecarboxylic esters, and exhibit the properties of the leucoauramines. They dissolve in glacial acetic acid to intensely blue solutions, and in neutral or acid solution they condense with tertiary aromatic amines giving triphenylmethane derivatives; thus a theoretical yield of ethyl hexamethyltriaminotriphenylacetate is obtained by warming a molecular mixture of dimethylaniline and ethyl aminotetramethyldiaminodiphenylacetate,

$$C_6H_5 \cdot NMe_2 + NH_2 \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot CO_2Et = C(C_6H_4 \cdot NMe_2)_3 \cdot CO_2Et + NH_3.$$

They are oxidised by potassium ferricyanide to the auramines $C(C_6H_4 \cdot NR_2)_2{:}NH$, which are precipitated in a pure condition. E. H.

Quinonoid Compounds. XII. Aniline-black. I.

RICHARD WILLSTÄTTER and CHARLES WATSON MOORE (*Ber.*, 1907, **40**, 2665—2689. Compare Nover, this vol., i, 262).—Caro (*Chem. Zeit.*, 1896, **21**, 840) obtained by the oxidation of aniline in aqueous alkaline solution a yellow substance, which he showed to be a quinonoid derivative of *p*-aminodiphenylamine. He drew the conclusion that the substance was benzoquinonephenyldi-imine, but a re-examination of the substance (m. p. 73—77°) shows it to be a mixture of this di-imine and the benzoquinonephenylmonoimine, which crystallise together in long, yellow needles; they may, however, be separated by using hexane as solvent, and on reduction the substance gives nearly equal amounts of *p*-hydroxy- and *p*-amino-diphenylamines.

p-*Benzoquinonemonomethyldi-imine*, $NMe\colon C_6H_4\colon NH$, best prepared by the oxidation of phenylenemethyldiamine by dry lead peroxide in boiling light petroleum (b. p. 35—40°), crystallises in colourless prisms, m. p. 64—67°. In one hour it changes into a brown-tarry mass. The *sulphate* is precipitated in long, colourless prisms from a petroleum solution of the imine on addition of an ethereal solution of the monohydrate; on warming the aqueous solution of the sulphate, *p*-benzoquinone is formed. An ethereal solution of hydrogen chloride gives a green precipitate which is not hydrolysed to benzoquinone by water. p-*Benzoquinonemonophenyldi-imine*, $NPh\colon C_6H_4\colon NH$, is obtained from an ethereal solution of *p*-aminodiphenylamine and dry silver oxide, and crystallises in light-yellow prisms, m. p. 88—90°; the substitution of the phenyl group for methyl results in a deepening of the colour. Its properties are similar to the other imines described; hot dilute sulphuric acid gives benzoquinone; hydroxylamine hydrochloride yields *p*-nitrosodiphenylamine.

The aqueous solution of benzoquinonephenyldi-imine, after a time, slowly deposits Bandrowski's quinonephenylmonoimine, m. p. 100—101° (Abstr., 1888, 943: m. p. 97°).

The *hydrochloride* of quinonephenyldi-imine, $C_{12}H_{10}N_2,HCl$, is brown, and in the course of one day polymerises to a mixture of green insoluble salts, the separation of which is accomplished by taking advantage of their different basicities. It is, however, easier to oxidise *p*-aminodiphenylamine by ferric chloride (Nietzki, *Ber.*, 1879, **12**, 1402), or, better still, by hydrogen peroxide in the presence of a small quantity of ferrous sulphate.

The emeraldine base, *azurine*, $C_{24}H_{20}N_4$, obtained in a well crystallised condition by first precipitating the crude base from its benzene solution by light petroleum, then reducing it to the leuco-base, and subsequent reoxidation, crystallises from hexane in deep blue, microscopic prisms, m. p. about 165°. It is strongly basic; the *hydrochloride* is bluish-green. A molecular weight determination by the freezing point method shows it to be a C_{24} derivative. The *leuco-base*, $C_{24}H_{22}N_4$, results along with black oxidation substances by heating with water in a sealed tube at 150—170° for five hours, or by redution with stannous chloride or phenylhydrazine. It crystallises in microscopic prisms, m. p. 185°.

On oxidation of the azurine in cold benzene solution by dry lead peroxide, a dark *red imine*, $C_{24}H_{18}N_4$, is obtained in leaflets. It is further purified by shaking quickly with very dilute acid and then liberating the base from the acid solution by ammonia; m. p. 195—196° with polymerisation. Hydrogen chloride forms the *compound*,

$$C_{24}H_{18}N_4,3HCl,$$

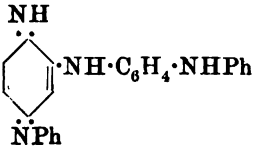
which is not, however, a true trihydrochloride, some of the chlorine being contained in the aromatic nucleus. This red imine, when heated with water at 150—170°, polymerises to a black, glistening mass, $(C_{24}H_{18}N_4)x$. A table is given comparing aniline-black and this "polymerisation-black" which show them to be very similar, but not identical. The polymerisation-black yields a *hydrochloride*, the aniline-black does not give a simple hydrochloride. An *acetyl* derivative is obtained from this new black. The conclusion is drawn that the molecular formula of aniline-black must be at least $C_{48}H_{36}N_8$.

Accompanying the red imine, obtained by oxidising the emeraldine base, there is 8—10% of a weaker base containing oxygen. This *red imine*, $C_{24}H_{17}ON_3$, does not form salts with $N/10$ acids, and crystallises in microscopic needles, m. p. 216—217°. It polymerises to an insoluble black substance when heated with water at 150—170°. The *leuco-base*, $C_{24}H_{21}ON_3$, obtained on reduction of the imine with phenylhydrazine, is colourless, m. p. 194—195°, and oxidises easily with atmospheric oxygen to a semi-quinonoid imine; with silver oxide it is further oxidised.

A second series of oxygen derivatives of emeraldine is obtained from the oxidation of mixture of *p*-hydroxy- and *p*-aminodiphenylamine with 3% hydrogen peroxide and a little ferrous sulphate. The operation is finished in five minutes. The *blue imine*, $C_{24}H_{19}ON_3$, is purified through its sulphate, and crystallises from a mixture of benzene and petroleum in rosettes of needles, m. p. 148—149°. It behaves towards water at 150—170° like emeraldine, partly giving rise to a leuco-base and partly to a black substance. Another *red imine* of composition $C_{24}H_{17}ON_3$ is obtained by oxidising the blue imine with lead peroxide; it is light red and has m. p. 222—223°. The *leuco-base*, $C_{24}H_{21}ON_3$, has m. p. 198—200°.

The paper concludes with a table giving the various colour changes which these imines undergo in alcohol, benzene, and sulphuric acid.

The constitution of the emeraldine bases cannot be of the nature of aminoazo-dyes. Although such condensations have been recognised in the case of the oxidation of *o*-phenylenediamine and benzidine (Abstr., 1905, i, 723; 1906, i, 996), the emeraldine bases do not contain the azo-group, as reduction of the leuco-bases cannot be effected under circumstances where the azo-bond would be broken. The blue imine may be



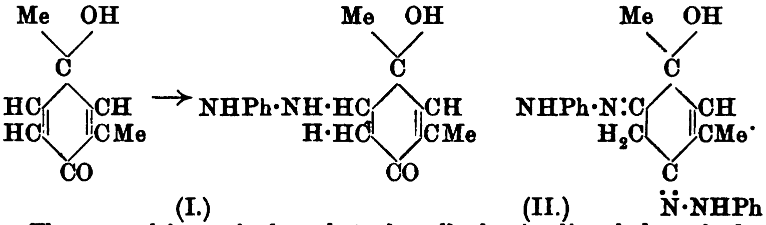
$$NPh{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2,$$

the red, $NPh{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N{:}C_6H_4{:}NH$; the annexed formula has been rejected as such a compound might be expected to yield an azine.

W. R.

Action of Phenylhydrazine on Ketonic 2 : 4-Dimethylquinol.

EUGEN BAMBERGER and EMIL REBER (*Ber.*, 1907, 40, 2258—2274. Compare this vol., i, 606).—The action of phenylhydrazine on ketonic xyloquinol differs according as hydroxyl ions are present or not. In the presence of hydroxyl ions, addition of the $NH{\cdot}NH{\cdot}C_6H_5$ group and the H atom takes place in positions 5 and 6 respectively, thus:

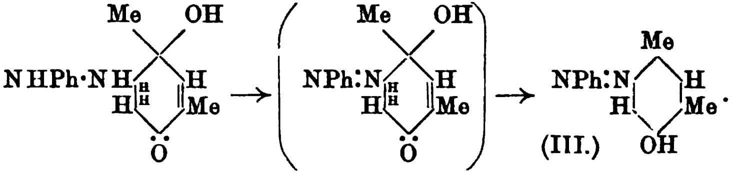


(I.) (II.)

The resulting hydroxyketophenylhydrazinodimethyltetrahydrobenzene (I) has the reactions typical of hydrazo-compounds.

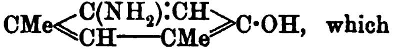
When the action of phenylhydrazine on xyloquinol is conducted in neutral (ethereal) solution, the main product of the action is the bisphenylhydrazone of a hydroxydiketodimethyltetrahydrobenzene (II).

Hydroxyketophenylhydrazinodimethyltetrahydrobenzene (formula I) forms silky needles, m. p. 213—213·5° (decomp.). It is readily soluble in mineral acids and is reprecipitated on the addition of alkali; it reduces Fehling's solution in the cold. Its *picrate*, $C_{20}H_{21}O_9H_5$, has m. p. 177° (decomp.). Its *oxalate*, $(C_{14}H_{18}O_2N_2)_2,C_2H_2O_4$, has m. p. 180° (decomp.). When oxidised by ferric chloride in dilute hydrochloric acid solution, the hydrazinoquinol is converted into 4-*benzeneazo*-6-*hydroxy*-1 : 3-*dimethylbenzene* (formula III), thus:

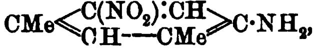


(III.)

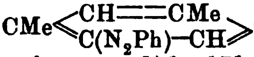
The latter forms orange-yellow, glistening needles, m. p. 113·5—114°. Its solution in concentrated sulphuric acid is red. It forms a *benzoyl* derivative, crystallising in orange-coloured, glistening needles or leaflets, m. p. 115—116°. The benzeneazoxylenol itself is reduced by aluminium amalgam to form 6-*amino*-4-*hydroxy*-1 : 3-*dimethylbenzene*,



$CMe{<}{\overset{C(NH_2){:}CH}{\underset{CH\text{——}CMe}{}}}{>}C{\cdot}OH$, which forms glistening needles or nacreous scales, m. p. 166·5—167°. In order to confirm the constitution assigned to the preceding compound, it was synthesised from nitro-*as*-*m*-xylidine,

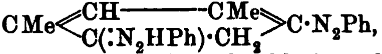


$CMe{<}{\overset{C(NO_2){:}CH}{\underset{CH\text{——}CMe}{}}}{>}C{\cdot}NH_2$, the amino-group being replaced by a hydroxy-group in the usual manner, and the resulting 6-nitro-4-hydroxy-1 : 3-dimethylbenzene then reduced by stannous chloride.

When ketonic xyloquinol is heated with phenylhydrazine for thirty-five to forty hours in the presence of ether, one of the products of the action is 1-benzeneazo-2 : 4-dimethylbenzene, which was identified by reducing it by zinc dust to the corresponding hydrazo-compound, m. p. 99·5—100°. The main product is, however, *hydroxydiketodimethyltetrahydrobenzene bisphenylhydrazone* (formula II), which separates from benzene, alcohol, or light petroleum in silky, orange-coloured needles, m. p. 168·5—169·5°. Its alcoholic solution does not reduce either Fehling's solution or silver oxide, but reduces silver nitrate slowly at the ordinary temperature. When oxidised by ferric chloride, it is converted into 4 : 6-*bisbenzeneazo*-1 : 3-*dimethylbenzene*,  $\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{=\!=}CMe}\\ \mathrm{C(N_2Ph){-}CH}\end{matrix}{>}\mathrm{C{\cdot}N_2Ph}$, which forms glistening, orange-red scales, m. p. 171—171·5°.

The latter compound, on reduction with aluminium amalgam, forms 1 : 3-xylylene-4 : 6-diamine.

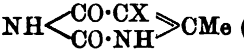
Benzeneazoketodimethyldihydrobenzene phenylhydrazone,



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{-\!-\!-\!-}CMe}\\ \mathrm{C(:N_2HPh){\cdot}CH_2}\end{matrix}{>}\mathrm{C{\cdot}N_2Ph},$$

may be obtained by adding a little hydrochloric acid to a concentrated solution of hydroxydiketodimethyltetrahydrobenzene bisphenylhydrazone in acetone as orange-coloured needles, m. p. 152·5—153·5°, the operation being conducted in an atmosphere of coal-gas. This compound is very readily oxidised to form the azo-compound with m. p. 171—171·5°, already described. A. McK.

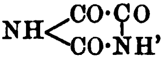
Oxidation of Uracil Derivatives. GUSTAV OFFE (*Annalen*, 1907, **353**, 267—283. Compare Behrend and Dietrich, Abstr., 1900, i, 120; Behrend and Thurm, Abstr., 1902, i, 832; Behrend and Fricke, Abstr., 1903, i, 739; Behrend and Hufschmidt, Abstr., 1906, i, 310; Hoebel, this vol., i, 557).—It has been shown previously that when oxidised with potassium permanganate equivalent to three atoms of oxygen in the cold, 4-methyluracil yields chiefly acetylcarbamide and oxalic acid, the hydrolysis products of acetyloxaluric acid, whereas if the reaction mixture is heated, the principal product is oxaluric acid, the hydrolysis product of parabanic acid, which is formed together with acetic acid. The oxidation of 5-substituted-4-methyluracils,



$$\mathrm{NH}{<}\begin{matrix}\mathrm{CO{\cdot}CX}\\ \mathrm{CO{\cdot}NH}\end{matrix}{>}\mathrm{CMe}\ (\mathrm{X = Br, NO_2, NH_2}),$$

has been studied now in the same manner. The products obtained are those formed from 4-methyluracil, but their relative amounts are found to depend largely on the nature of the substituting group. 5-Bromo- and 5-nitro-4-methyluracils yield acetylcarbamide together with little oxaluric acid, the proportion between the amounts of the products being almost the same if the oxidation takes place in cold or in boiling solution. 5-Amino-4-methyluracil, on the other hand, resembles 4-methyluracil, yielding acetylcarbamide together with smaller amounts of oxaluric acid when oxidised in the cold, but oxaluric acid as the chief product when oxidised in boiling solution. This difference in behaviour is ascribed to the pronounced acid nature of the bromo- and nitro-methyluracils, in consequence of which the formation of free alkali and therefore the conversion of the intermediately formed methyl*iso*dialuric acid, or the corresponding bromo- and nitro-derivatives, into acetylallanturic acid is prevented. In agreement with this, acetyloxaluric acid, $\mathrm{NHAc{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CO_2H}$, is obtained from 5-bromo-, 5-nitro, and 5-amino-methyluracils if the formation of free alkali during the oxidation is prevented entirely.

It is shown that when hydrolysed with alkalis or when boiled in neutral or slightly acid solution, acetyloxaluric acid yields acetylcarbamide and oxalic acid, but that oxaluric acid is not formed. This is of importance as showing that the oxaluric acid, obtained on oxidation of 4-methyluracil, must be derived wholly from intermediately formed parabanic acid,



$NH<\begin{matrix}CO\cdot CO\\ CO\cdot NH\end{matrix}$, this five atom-ring being formed by oxidation of the six atom pyrimidine ring of the uracil.

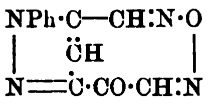
Derivatives of uracil undergo oxidation in a manner similar to those of 4-methyluracil; the intermediate product is *formyloxaluric acid*, $CHO\cdot NH\cdot CO\cdot NH\cdot CO\cdot CO_2H$, which differs from acetyloxaluric acid in that on hydrolysis it yields formic acid and oxaluric acid. Formyloxaluric acid has been isolated from the oxidation products of *iso*barbituric acid, 5-nitrouracil, and 5-aminouracil hydrochloride; only the final product, oxaluric acid, was obtained from 5-carbamidouracil (hydroxyxanthine).

Potassium formyloxalurate, $C_4H_3O_5N_2K$, crystallises from water in small needles containing about $\frac{1}{2}H_2O$, which is lost at 120°; the anhydrous salt decomposes at 208·5°. G. Y.

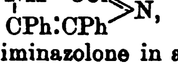
Transformation of Pyrroles into Derivatives of Pyrazole. VICENZO CASTELLANA (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 767—775. Compare Abstr., 1905, i, 941).—The author gives details of the work previously published (*loc. cit.*), and describes the means adopted to establish the constitutions of the products obtained.

When the ketone, m. p. 90°, is treated with potassium permanganate in presence of alkali, one of the following two compounds is obtained according to the conditions of the reaction. (1) 1-Phenyl-5-methylpyrazole-3-carboxylic acid (compare Claisen and Roosen, Abstr., 1891, 1106); (2) 1-phenylpyrazole-3 : 5-dicarboxylic acid (compare Balbiano, Abstr., 1890, 1164). The ketone hence has the constitution previously suggested for it (*loc. cit.*).

When treated with amyl nitrite (1 mol.) in presence of sodium ethoxide, the ketone (1 mol.) yields an iso*nitroso*-derivative, $C_{12}H_{11}O_2N_3$, which crystallises from benzene in small, almost white, hard needles, m. p. 172°, whilst the use of double the above proportion of amyl nitrite leads to the formation of the *anhydride* of the di*isonitroso*-derivative (annexed formula), which crystallises from benzene in minute needles, m. p. 175°, and is soluble in alkalis, from which it is reprecipitated by carbon dioxide. T. H. P.



Diphenylglyoxaline and ψ-Chlorodiphenylglyoxaline. HEINRICH BILTZ (*Ber.*, 1907, 40, 2630—2636).—A new method of preparing diphenylglyoxaline (compare Pinner, Abstr., 1905, i, 476). Although 4 : 5-diphenyliminazolone (Abstr., 1905, i, 674) cannot be directly reduced by phosphorus and hydriodic acid, the reduction to the glyoxaline may be accomplished almost quantitatively in two stages. 2-*Chloro*-4 : 5-*diphenylglyoxaline*,



$\begin{matrix}NH-CCl\\ CPh:CPh\end{matrix}>N$, prepared by heating phosphoryl chloride and diphenyliminazolone in a sealed tube at 140°

for four hours, crystallises in colourless, slender needles, m. p. 217·5°, and is easily reduced to diphenylglyoxaline by zinc and hydrochloric acid. Diphenyliminazolone cannot be regenerated from the chloro-compound by heating with hydrochloric acid or by silver oxide. Heating with 10% nitric acid results in its hydrolysis to benzil and carbamide.

2-Chloro-4 : 5-diphenylglyoxaline does not form salts with weak acids like oxalic and picric acid; the *hydrochloride* has m. p. 167—168°; the *hydrogen sulphate*, m. p. 123—124° (decomp.). *2-Chloro-3-acetyl-4 : 5-diphenylglyoxaline*, $C_{17}H_{13}ON_2Cl$, m. p. 185°, is easily hydrolysed by water or alcohol.

The following salts of diphenylglyoxaline are described: the hydrochloride has no m. p. as it loses hydrogen chloride at 140° (Pinner, Abstr., 1903, i, 123, gives m. p. 202°); the *sulphate*, *nitrate*, decomposes explosively at 164°, *oxalate*, decomp. at 244°, and *picrate* has m. p. 135°. *3-Acetyl-4 : 5-diphenylglyoxaline*, $C_{17}H_{14}ON_2$, crystallises in colourless needles, m. p. 149·5°. It is more stable than the 2-chloro-compound, but slowly decomposes in water into the acetate.

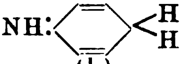
Oxidation of diphenylglyoxaline with potassium permanganate in acid solution yields dibenzoylcarbamide.

An *additive* compound of diphenylglyoxaline and hydroxydiphenyltriazine is formed by mixing their ethyl acetate solutions, and crystallises in light yellow needles, m. p. 184—185°. The chloro-compound does not yield an additive product. W. R.

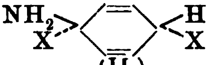
Explanation of the Formation of Quinoneimine Dyes from Amines by Oxidising and Halogen Fusions.

ADRIANO OSTROGOVICH and T. SILBERMANN (*Chem. Zentr.*, 1907, i, 1194; from *Bul. Soc. Sci. Bucuresci*, 15, 281—302).—It having been found that indulines are formed if anilines are heated with halogens or substances which yield free halogens, as ethylene iodide, it was sought to form rosaniline and chrysaniline dyes in the same manner, since whilst oxidation of aniline leads to the formation of induline, rosaniline dyes are formed if *p*-toluidines are present. Although chlorine, bromine, and iodine give similar results in the induline formation, only iodine is capable of forming rosaniline from a mixture of aniline with *o*- and *p*-toluidines, whilst chlorine converts the aniline into induline and the *p*-toluidine into chrysaniline.

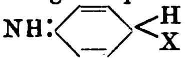
Any explanation of the formation of induline by oxidation or by the action of halogens must include that of the intermediate product, benzoquinoneimine. The halogens cannot act as oxidising agents, as the reaction takes place with a quarter of the halogen necessary for oxidation of the hydrogen atoms; moreover, the halogens are oxidising agents only in presence of water or alkalis. It is assumed that the aniline acts in the quinone form I, giving with halogens the hypothetical intermediate substances II, III, and IV. Benzoquinoneiminephenylimine is then formed by the action of aniline on IV, or possibly on III, which would account for the liberation of hydrogen during the reaction and for the small amount of halogen required.



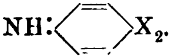
(I.)



(II.)



(III.)



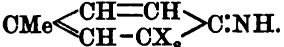
(IV.)

Benzoquinonediphenylimine is formed by the action of aniline on the quinoneimidephenylimine.

It is shown that the formation of indulines from *p*-halogenoanilines and aniline hydrochlorides takes place, not directly, but in consequence of the liberation of the halogen by decomposition of the halogenoaniline.

The formation of rosaniline from aniline and *p*-toluidine is explained usually as resulting from oxidation of the toluidine to *p*-aminobenzaldehyde and condensation of this with the aniline; it is argued, contrary to this view, that the first products of the reaction are benzoquinoneimine and *p*-aminobenzyl alcohol, which condense with unchanged aniline. In the action of iodine on a mixture of aniline and *p*-toluidine, the intermediate products are analogously di-iodobenzoquinoneimine and *p*-aminobenzyl alcohol. Brunner and Brandenburg's formation of methyl violet from *p*-bromodimethylaniline is explained in the same manner (Abstr., 1878, 314).

Chrysaniline must be formed by condensation of aniline with *p*-aminobenzyl alcohol and an *o*-benzoquinoneimine derived from *p*-toluidine,



$$\mathrm{CMe}{<}\genfrac{}{}{0pt}{}{\mathrm{CH{=}CH}}{\mathrm{CH{-}CX_2}}{>}\mathrm{C{:}NH}.$$

Induline dyes are formed by heating aniline with iodine or with chlorine at 180°, or by heating aniline at 180° with aniline hydrochloride which has been oxidised with air, lead dioxide, persulphate, &c. G. Y.

Preparation of Magenta and Ortho- and Meta-halogen Magentas by Means of Iodine. T. Silbermann and Adriano Ostrogovich (*Chem. Zentr.*, 1907, i, 1197; from *Bul. Soc. Sci. Bucuresci*, 15, 303—307. Compare preceding abstract).—Paramagenta is prepared by adding 60 grams of iodine to a solution of 22 of *p*-toluidine in 38 of aniline, gradually raising the temperature to 180° and maintaining it at this point until the mass becomes solid. Magenta is prepared in a similar way, using 19 grams of aniline, 22 of toluidine, and 60 of iodine. When *p*-bromoaniline is heated with *p*-toluidine, induline, chrysaniline, and chrysotoluidine are formed, but if a trace of iodine is added, magenta is practically the only product. Nitroaniline yields only chrysaniline. Ortho- and meta-halogen derivatives of magenta have been prepared from the corresponding substituted anilines. All the halogen derivatives are very sparingly soluble in water. o-*Dichloroparamagenta* does not crystallise, but has all the properties of a magenta derivative; o-*dibromoparamagenta* resembles the corresponding, chloro-derivative. In the preparation of m-*dichloro-* and m-*dibromo-paramagenta*, rather large quantities of chrysaniline are formed and can be isolated by extracting with ether.

E. W. W.

Relations between the Constitution, Colour, and Absorption Spectra of the Triphenylmethane Dyes. Fritz Reitzenstein and Walther Schwerdt (*J. pr. Chem.*, 1907, [ii], 75, 369—415. Compare Abstr., 1905, i, 300; 1906, i, 316).—In continuation of the investigation into the influence of substituting groups on the shade of dyes of the triphenylmethane series (*loc. cit.*), a number of leuco-bases, $CH(C_6H_4NMe_2)_2 \cdot C_6H_2MeR \cdot NH_2$ and $CH(C_6H_3Me \cdot NMe_2)_2 \cdot C_6H_2MeR \cdot NH_2$ [$R = NO_2$, Cl, or SO_3H] have been prepared by condensation of chloro-, nitro-, and sulphotoluidines with tetramethyldiaminobenzhydrol and tetramethyldiaminoditolylhydrol, and converted into products of the types $CH(C_6H_4NMe_2)_2 \cdot C_6H_3Me \cdot N:CH \cdot CH:CH \cdot CH:CH \cdot NH_2Cl \cdot C_6H_3Me - \cdot CH(C_6H_4NMe_2)_2$ by the action of dinitrophenylpyridinium chloride (Abstr., 1906, i, 316), and $CH(C_6H_4NMe_2)_2 \cdot C_6H_3Me \cdot NH \cdot CH:CH - \cdot CH:NHCl \cdot C_6H_3Me \cdot CH(C_6H_4NMe_2)_2$ by the action of propiolaldehyde diethylacetal (compare Claisen, Abstr., 1904, i, 14). Compounds of the former type could not be obtained from the leuco-bases derived from the nitrotoluidines. The corresponding dyes are obtained by oxidation of the leuco-bases by chloranil in alcoholic-acetic acid solution. The examination of the absorption spectra of the dyes by Formánek's method shows that, in agreement with Noelting's rule, the condensation of tetramethyldiaminobenzhydrol with substituted toluidines leads, in general, to the formation of isomeric leuco bases, the constitution of the product depending on whether the condensation takes place in hydrochloric or sulphuric acid solution, but that the products obtained from *p*-chloro-*o*-toluidine and tetramethyldiaminobenzhydrol by the two methods of condensation are identical, having identical absorption spectra, as have also the dianilides obtained from them by the action of dinitrophenylpyridinium chloride; nevertheless, the substances have different melting points.

It is found that the shade of the simple triphenylmethane dyes, derived from tetramethyldiaminobenzhydrol, is weakened by a nitro-group in the ortho-, but, contrary to Reitzenstein and Runge's statement (Abstr., 1905, i, 300), is intensified by a nitro-group in the meta-position. The colour of the dye becomes pure and more intense on introduction of a chlorine atom into the ortho-, is intensified if the chlorine atom assumes the meta-, and becomes deeper and clearer if the chlorine is introduced into the para-position. The introduction of the sulpho-group into the ortho-position results in a weakening of the shade which changes towards the green; into the meta-position, in weakening of the shade which becomes less clear; and into the para-position, in intensification of the colour.

The dyes obtained from tetramethyltriaminoditolylhydrol have weaker colours; in consequence of their feeble dyeing properties, the influence of the position of the nitro-, chloro-, and sulpho-groups cannot be observed.

The dyes in which two tetramethyltriaminotriphenylmethane groups are united by a five carbon atom-chain have stronger shades than the simple dyes; the colour is further intensified by the introduction of a chlorine atom. The union of two molecules of a simple dye by a three carbon atom-chain results in a change from blue to light green.

The wave-lengths given in the following description are those of the bands in the absorption spectra of the leuco-bases.

The following leuco-bases are derived from tetramethyldiaminobenzhydrol by condensation with the substituted toluidines mentioned, in sulphuric or hydrochloric acid as stated; the substituted groups, the positions of which are given, are those in the phenyl nucleus derived from the toluidine. The hydrochlorides are the products of the action of dinitrophenylpyridinium chloride on the simple leuco-bases.

m-Nitro-*p*-toluidine (sulphuric acid) $[NO_2 : NH_2 : Me = 2 : 3 : 6]$: green powder, m. p. 208°, $\lambda = 617{\cdot}50$, yields a green *dye*. *m*-Nitro-*p*-toluidine (hydrochloric acid) $[NO_2 : NH_2 : Me = 3 : 2 : 5]$: yellow precipitate, $\lambda = 595{\cdot}38$, yields a blue *dye*. *p*-Nitro-*m*-toluidine (sulphuric acid) $[NO_2 : NH_2 : Me = 2 : 3 : 5]$: whitish-grey powder, $\lambda = 661{\cdot}36$, yields a green *dye*. *p*-Nitro-*m*-toluidine (hydrochloric acid) $[NO_2 : NH_2 : Me = 5 : 4 : 2]$: dull-green powder, $\lambda = 602{\cdot}14$, yields a *dye* which dyes tannin-mordanted cotton blue. *o*-Chloro-*p*-toluidine (sulphuric acid) $[Cl : NH_2 : Me = 5 : 3 : 6]$: brown powder, $\lambda = 632{\cdot}15$, yields a *dye* which dyes tannin-mordanted cotton green; the *hydrochloride* forms a red, crystalline powder; the *base*, $C_{58}H_{60}ON_6Cl_2$, is soluble in carbon disulphide, $\lambda = 639{\cdot}50$, yields a *dye* which dyes tannin-mordanted cotton a dark green. *o*-Chloro-*p*-toluidine (hydrochloric acid) $[Cl : NH_2 : Me = 4 : 2 : 5]$: grey powder, m. p. about 100°, $\lambda = 613{\cdot}4$, yields a *dye* which dyes tannin-mordanted cotton dark blue; the *hydrochloride*, $C_{58}H_{59}N_6Cl_3$, forms orange crystals, $\lambda = 655{\cdot}60$, yields a *dye* which dyes tannin-mordanted cotton a dark blue. *p*-Chloro-*m*-toluidine (sulphuric acid) $[Cl : NH_2 : Me = 2 : 3 : 5]$: light grey, $\lambda = 614{\cdot}50$, after oxidation dyes tannin-mordanted cotton blue; the *hydrochloride* yields a *base*, which is obtained as an orange-red powder, m. p. 110°, $\lambda = 620{\cdot}70$, and after oxidation dyes mordanted cotton dark blue. *p*-Chloro-*m*-toluidine (hydrochloric acid) $[Cl : NH_2 : Me = 5 : 4 : 2]$: greyish-blue, crystalline powder, m. p. 177°, $\lambda = 611{\cdot}50$, yields a blue *dye*; the *base*, obtained from the *hydrochloride*, m. p. about 105°, $\lambda = 612{\cdot}10$, after oxidation dyes tannin-mordanted cotton dark blue. *m*-Chloro-*p*-toluidine (sulphuric acid) $[Cl : NH_2 : Me = 4 : 3 : 6]$: bluish-grey powder, m. p. 170°, $\lambda = 620{\cdot}38$, yields a bluish-green *dye* which dyes mordanted cotton green; the *hydrochloride* forms yellow, flocculent crystals, m. p. 175°; the *base*, $\lambda = 640{\cdot}20$, after oxidation dyes mordanted cotton dark green. *m*-Chloro-*p*-toluidine (hydrochloric acid) $[Cl : NH_2 : Me = 3 : 2 : 5]$: m. p. 105°, $\lambda = 594{\cdot}60$, yields a blue *dye*; the *base*, derived from the *hydrochloride*, $\lambda = 605{\cdot}50$, after oxidation dyes mordanted cotton blue. *p*-Chloro-*o*-toluidine (sulphuric acid) $[Cl : NH_2 : Me = 5 : 3 : 2]$: blue powder, m. p. 154°, $\lambda = 617{\cdot}64$, yields a blue *dye*; the *base*, m. p. 105°, $\lambda = 514{\cdot}20$, derived from the *hydrochloride*, yields a blue *dye*. *p*-Chloro-*o*-toluidine (hydrochloric acid) $[Cl : NH_2 : Me = 2 : 4 : 5]$: m. p. 210°, $\lambda = 617{\cdot}50$, after oxidation dyes mordanted cotton reddish-blue; the *hydrochloride* is red, and yields a *base*, m. p. 184°, $\lambda = 514{\cdot}20$, which after oxidation dyes mordanted cotton dark blue. *p*-Sulpho-*o*-toluidine (sulphuric acid) $[SO_3H : NH_2 : Me = 5 : 3 : 2]$: m. p. 70°, $\lambda = 632{\cdot}50$, yields a green *dye*. *p*-Sulpho-*o*-toluidine (hydrochloric acid) $[SO_3H : NH_2 : Me = 2 : 4 : 5]$: m. p. 210°, $\lambda = 617{\cdot}20$, yields a bluish-green *dye*. *o*-Sulpho-*p*-toluidine (sulphuric acid) $[SO_3H : NH_2 : Me = 5 : 3 : 6]$: $\lambda = 632{\cdot}15$, yields a green *dye*. *o*-Sulpho-*p*-toluidine (hydrochloric acid) $[SO_3H : NH_2 : Me = 4 : 2 : 5]$: sinters at 130°, $\lambda = 590{\cdot}75$, after oxidation dyes mordanted cotton blue.

The following similar substances are prepared from tetramethyldiaminoditolylhydrol by condensation with substituted toluidines; the positions of the substituting groups in the toluidine nucleus are given.

m-Nitro-*p*-toluidine (sulphuric acid) [$NO_2:NH_2:Me=2:3:6$]: brown powder, yields a green *dye*. *m*-Nitro-*p*-toluidine (hydrochloric acid) [$NO_2:NH_2:Me=3:2:5$]: yellow powder, resinifies and becomes green on exposure to air, after oxidation dyes mordanted cotton blue. *p*-Nitro-*m*-toluidine (sulphuric acid) [$NO_2:NH_2:Me=2:3:5$]: brown precipitate, after oxidation dyes mordanted cotton a weak light green. *p*-Nitro-*m*-toluidine (hydrochloric acid) [$NO_2:NH_2:Me=5:4:2$]: brown powder, yields a green *dye*. *o*-Chloro-*p*-toluidine (sulphuric acid) [$Cl:NH_2:Me=5:3:6$]: brown precipitate, after oxidation dyes mordanted cotton dull green; the *hydrochloride* dissolves in carbon disulphide, and yields a free *base*, $C_{55}H_{64}ON_6Cl_2$, which is orange, and after oxidation dyes mordanted cotton green. *o*-Chloro-*p*-toluidine (hydrochloric acid) [$Cl:NH_2:Me=4:2:5$], brown mass, yields a dull green *dye*; the *hydrochloride* yields a blue *dye*. *p*-Chloro-*m*-toluidine (sulphuric acid) [$Cl:NH_2:Me=2:3:5$]: grey becoming black, after oxidation dyes mordanted cotton brown; a dianilide hydrochloride could not be obtained. *p*-Chloro-*m*-toluidine (hydrochloric acid) [$Cl:NH_2:Me=5:2:4$]: yields a dull green *dye*; the *hydrochloride* forms a reddish-brown powder, sinters at 85°, yields a weak green *dye*. *m*-Chloro-*p*-toluidine (sulphuric acid) [$Cl:NH_2:Me=4:3:6$]: on oxidation yields a brown solution; the hydrochloride is brown, and yields a weak green *dye*. *m*-Chloro-*p*-toluidine (hydrochloric acid) [$Cl:NH_2:Me=3:2:5$]: brownish-yellow, yields a weak blue *dye*; the *hydrochloride*, $C_{57}H_{67}N_6Cl_3$, yellowish-red substance, m. p. 95°, yields a blue *dye*. *p*-Chloro-*o*-toluidine (sulphuric acid) [$Cl:NH_2:Me=5:3:2$]: brown powder, yields a weak green *dye*; the *base*, from the *hydrochloride*, is obtained as a brownish-yellow powder, and yields a weak green *dye*. *p* Chloro-*o*-toluidine (hydrochloric acid) [$Cl:NH_2:Me=2:4:5$]: brown, crystalline powder, yields a dull green *dye*; the *hydrochloride* is obtained as a reddish-brown powder, after oxidation dyes mordanted cotton a weak blue. *p*-Sulpho-*o*-toluidine (sulphuric acid) [$SO_3H:NH_2:Me=5:3:2$]: light brown powder. *p*-Sulpho-*o*-toluidine (hydrochloric acid) [$SO_3H:NH_2:Me=2:4:5$]: grey precipitate. *o*-Sulpho-*p*-toluidine (sulphuric acid) [$SO_3H:NH_2:Me=5:3:6$]: brown powder, m.p. about 140°, on oxidation yields a green solution. *o*-Sulpho-*p*-toluidine (hydrochloric acid) [$SO_3H:NH_2:Me=4:2:5$]: light grey, crystalline powder, m. p. above 220°.

When heated on the water-bath with propiolaldehyde diethylacetal in 38% aqueous hydrochloric acid, the leuco-base, obtained by condensation of tetramethyldiaminobenzhydrol and *p*-toluidine in sulphuric acid solution, yields a yellowish-green *hydrochloride*, from which the *base*, $C_{51}H_{59}N_6\cdot OH$, m. p. 170°, $\lambda=625\cdot18$, is liberated by ammonia. After oxidation, it dyes cotton mordanted with tannin and tartar emetic, a grass-green. G. Y.

1:2-Naphthaquinone-4-sulphonic Acid. III. Franz Sachs and Erich Berthold (*Zeit. Farb. Ind.*, 1907, 6, 141—143. Compare this vol., i, 426).—The readiness with which 1:2-naphthaquinone-

4-sulphonic acid condenses with substances containing a primary amino-group has been utilised as a means of ascertaining the structure of the following compounds.

Auramine is shown to be $C(C_6H_4\cdot NMe_2)_2{:}NH,HCl$ by its combining with the sulphonic acid to form the *salt*

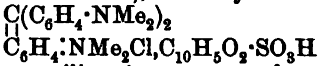
$$C(C_6H_4\cdot NMe_2)_2{:}NH,C_{10}H_5O_2\cdot SO_3H,$$

instead of condensing with the quinone as would happen if it had the structure $NMe_2Cl{:}C_6H_4{:}C(C_6H_4\cdot NMe_2)\cdot NH_2$; the salt obtained crystallises from alcohol in bluish-black needles, m. p. 200°.

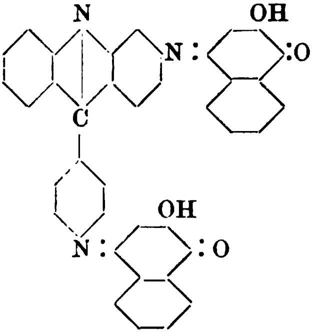
Brilliant-green in a similar manner gives the *salt*,

$$NEt_2\cdot C_6H_4\cdot CPh{:}C_6H_4{:}NEt_2Cl,C_{10}H_5O_2,SO_3H$$

(m. p. 118—120°), and crystal-violet the salt



$$\begin{array}{l}C(C_6H_4\cdot NMe_2)_2\\ \|\\ C_6H_4{:}NMe_2Cl,C_{10}H_5O_2\cdot SO_3H\end{array}$$



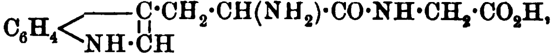
Chrysaniline, however, condenses with 2 mols. of the naphthaquinonesulphonic acid giving the annexed compound, which separates from nitrobenzene in the form of a crimson, crystalline powder.

In the case of *p*-rosaniline, only two of the three amino-groups condense with 1 : 2-naphthaquinone-4-sulphonic acid even in presence of an excess of the latter. W. A. D.

Synthesis of Polypeptides. XX. Derivatives of Tryptophan.

EMIL ABDERHALDEN and MARTIN KEMPE (*Ber.*, 1907, 40, 2737—2750).—The methods described previously have been extended to the preparation of polypeptides from tryptophan. The tryptophan used was prepared by Hopkins and Cole's method (Abstr., 1902, i, 193) from casein and had $[\alpha]_D^{20}$ +6·06° in water and +1·31° in normal hydrochloric acid.

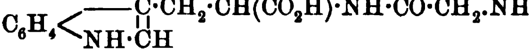
Tryptophan was converted into the *chloride* by Fischer's method; this at once coupled with glycine ethyl ester, and the dipeptide separated by means of the mercury sulphate double salt. *Tryptophylglycine*,



$$C_6H_4\Big<\begin{array}{l}\text{——}C\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,\\ NH\cdot \overset{\|}{C}H\end{array}$$

crystallises in colourless, microscopic needles, m. p. 180° (corr.), $[\alpha]_D^{20}$ +78·7°.

Chloroacetyl-d-*tryptophan*, prepared by the condensation of tryptophan with chloroacetyl chloride in presence of sodium hydroxide, forms glistening platelets, m. p. 159° (corr.), $[\alpha]_D^{20}$ −32·9°. *Glycyl*-d-*tryptophan*,



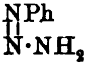
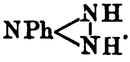
$$C_6H_4\Big<\begin{array}{l}\text{——}C\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2.NH_2,\\ NH\cdot \overset{\|}{C}H\end{array}$$

separates in small, equilateral, triangular plates, m. p. 302° (corr.), $[\alpha]_D^{20}$ +21·45°, and has a bitter taste.

As crystalline products could not be obtained from tryptophan with *dl*-leucine or *dl*-alanine, it was condensed with *d*-*α*-bromopropionyl chloride to d-*α*-*bromopropionyl*-d-*tryptophan*, which softens at 65° and melts at 72°. d-*Alanyl*-d-*tryptophan* is very soluble in water, has a bitter taste, decomposes at about 150° (corr.), $[\alpha]_D^{20}$ + 18·65°, and forms a well-crystallised, copper salt. d-*α-Bromo*iso*hexoyl*-d-*tryptophan* crystallises in needles, m. p. 118° (corr.), $[\alpha]_D^{20}$ +27·1°. l-*Leucyl*-d-*tryptophan* forms colourless, microscopic, hair-like, matted needles, which sinter at 130°, m. p. 148° (corr., decomp.), and taste bitter with a sweet after-taste; they have $[\alpha]_D^{20}$ +4·48°.

d-*α-Bromo*iso*hexoylglycyl*-d-*tryptophan*, prepared by condensing glycyltryptophan in the usual manner, sinters at 60°, m. p. 90—98°, $[\alpha]_D^{20}$ +54·47°. The tripeptide, l-*leucylglycyl*-d-*tryptophan*, forms a colourless, amorphous, sparingly soluble mass (decomp. 234°, corr.), $[\alpha]_D^{20}$ +32·30°. E. F. A

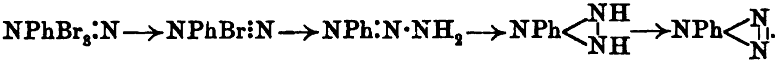
Phenyltriazen (Diazobenzeneamide). Otto Dimroth (*Ber.*, 1907, **40**, 2376—2389. Compare Abstr., 1903, i, 450; 1905, i, 311, 618; this vol., i, 21).—*Phenyltriazen*, the preparation of which is described in this paper, is of great interest as the first monosubstituted triazen. Although it is formed probably as the first product of the action of diazobenzene salts on ammonia, which leads finally to the formation of bisdiazobenzeneamide, all attempts to isolate it from the reacting mixture have been unsuccessful. It has been obtained, however, by reduction of phenylazoimide (compare Griess, *Annalen*, 1866, **137**, 77; Curtius, Abstr., 1896, i, 34; 1900, ii, 474) by means of stannous chloride and hydrogen chloride in ethereal solution at −20°. The resulting *stannichloride* is stable only in contact with ether at low temperatures, decomposes on evaporation of the ether or, with evolution of nitrogen, on treatment with water or alcohol, and yields the free base when stirred with 20% sodium hydroxide and ether at −18°.

Phenyltriazen, N_3H_2Ph, purified by conversion into its stable copper derivative and liberation by means of potassium cyanide below −18°, crystallises from a mixture of ether and light petroleum in colourless, pointed leaflets, m. p. 50° (decomp.), is stable in solution only below −15°, and decomposes when solid at the ordinary temperature, or when treated with solvents at the ordinary temperature, or with acids at low temperatures, developing heat and forming aniline and nitrogen. When spread in a thin layer on a porous plate, the leaflets change in five to ten minutes into small, indistinct crystals, m. p. 40° (decomp. evolving gas); this second *modification* is more stable, and when dissolved in ether at −18° and precipitated with light petroleum is retransformed into the modification crystallising in leaflets. The nature of the modifications is discussed and it is concluded that they are stereoisomerides,  $\begin{array}{l}\text{NPh}\\ \| \\ \text{N}\cdot\text{NH}_2\end{array}$ and $\begin{array}{r}\text{Ph.N}\\ \| \\ \text{N}\cdot\text{NH}\end{array}$, or more probably, the desmotropic forms, $NPh\!:\!N\cdot NH_2$ and  $NPh\!<\!\begin{array}{l}NH\\ |\\ NH\end{array}$.

The *copper* derivative, $C_6H_6N_3Cu$, formed by shaking phenyltriazen with cuprous chloride in ethereal solution at −15°, crystallises from much boiling benzene or chloroform in yellow prisms with strong electrical properties, decomposes without melting at high temperatures, is stable at the ordinary temperature when pure, and is decomposed by concentrated sulphuric acid, hot ammonia, or pyridine. The *silver* derivative forms unstable, pale yellow needles, decomposes when dried, and yields an odour of phenylazoimide on treatment with ammonia or sodium hydroxide.

The action of phenylcarbimide on phenyltriazen in ethereal solution leads to the formation of a *carbamide*, which on treatment with methyl iodide and sodium methoxide yields *s*-phenylmethylcarbamidoazobenzene (Abstr., 1905, i, 311).

Phenylcarbamidoazobenzene, $NHPh\cdot CO\cdot NH\cdot N{:}NPh$, crystallises in needles having strong electrical properties, m. p. 141°, has pronounced acid properties, and is decomposed by hot dilute hydrochloric acid yielding an odour of phenylcarbimide. The *sodium*, *potassium*, and *silver*, $C_{13}H_{11}ON_4Ag$, salts are described. Phenyltriazen is oxidised readily and quantitatively to phenylazoimide by means of sodium hypobromide or alkaline silver solutions; this action is employed to explain the formation of phenylazoimide from diazobenzene perbromide and ammonia:

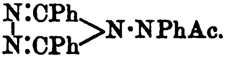


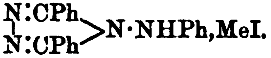
$$\mathrm{NPhBr_2{:}N \longrightarrow NPhBr{:}N \longrightarrow NPh{:}N\cdot NH_2 \longrightarrow NPh\lt\begin{matrix}NH\\ |\\ NH\end{matrix} \longrightarrow NPh\lt\begin{matrix}N\\ \|\\ N\end{matrix}}.$$

Small amounts of phenylazoimide are recognised best by conversion into 5-amino-1:4-diphenyl-1:2:3-triazole, m. p. 179° (169°: Abstr., 1903, i, 129). When oxidised by potassium permanganate at −15°, phenyltriazen yields a strong odour of *iso*nitrile, but not phenylazoimide.

The action of benzaldehyde on phenyltriazen in ethereal solution at −15° leads to the formation of benzylideneaniline and nitrogen. With β-naphthol, phenyltriazen evolves nitrogen and does not form benzeneazo-β-naphthol. G. Y.

Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXIV. *N*-Aminotriazole (*s*-Dihydrotetrazine).

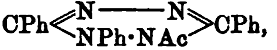
ROBERT STOLLÉ (*J. pr. Chem.*, 1907, [ii], 75, 416—432. Compare this vol., i, 359).—It is found now that the substance formed together with 1:3:6-triphenyl-1:2-dihydro-1:2:4:5-tetrazine by the action of phenylhydrazine on dibenzoylhydrazide dichloride and previously assumed to be 1:3:6-triphenyl-1:4-dihydro-1:2:4:5-tetrazine (Abstr., 1906, i, 462), yields an acetyl derivative which is identical with the condensation product of *as*-acetylphenylhydrazide and dibenzoylhydrazide dichloride, and must be therefore 1-*acetylanilino*-2:5-*diphenyl*-1:3:4-*triazole*,  $\mathrm{\begin{matrix}N{:}CPh\\ |\\ N{:}CPh\end{matrix}\gt N\cdot NPhAc}$. This result supports Bülow's view that the supposed *s*-dihydrotetrazines are *N*-amino-1:3:4-triazoles (Abstr., 1906, i, 905; this vol., i, 99). The feeble basic character of these substances (Pinner, Abstr., 1898, i, 94) is ascribed to the *as-sec.*-hydrazide grouping: $NH_2\cdot N(CR{:})_2$, it being well known that the basic properties of hydrazine are greatly diminished already in the primary hydrazides. It was proposed to bring further evidence as to the constitution of the *N*-aminotriazoles by, on the one hand, elimination of the methyl group from 1-methylanilino-2:5-di-*p*-bromophenyl-1:3:4-triazole formed by the action of *as*-phenylmethylhydrazine on di-*p*-bromobenzoylhydrazide dichloride, and, on the other, by the methylation of 1-anilino-2 : 5-diphenyl-1 : 3 : 4-triazole. This, however, could not be accomplished, since attempts in the first direction resulted in the elimination of the group ·NPhMe with formation of 2 : 5-di-*p*-bromophenyl-1 : 3 : 4-triazole, and in the second, in the formation of only the methiodide,



$\left.\begin{matrix}\mathrm{N{:}CPh}\\ \mathrm{N{:}CPh}\end{matrix}\right>\mathrm{N\cdot NHPh,MeI}$.

1-*Acetylanilino*-2 : 5-*diphenyl*-1 : 3 : 4-*triazole*, $C_{22}H_{18}ON_4$, crystallises in colourless prisms, m. p. 180°, and when boiled with aqueous sodium carbonate solution is hydrolysed, forming 1-anilino-2 : 5-diphenyl-1 : 3 : 4-triazole. In connexion with the formation of the acetyl compound, it is shown that *as*-acetylphenylhydrazine remains unchanged when heated with benzene in a sealed tube at 140°.

2-*Acetyl*-1 : 3 : 6-*triphenyl*-1 : 2-*dihydro*-1 : 2 : 4 : 5-*tetrazine*,



$$\mathrm{CPh}\left<\begin{matrix}\mathrm{N}\text{———}\mathrm{N}\\ \mathrm{NPh\cdot NAc}\end{matrix}\right>\mathrm{CPh},$$

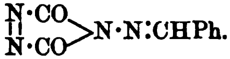
formed from triphenyl-1 : 2-dihydrotetrazine, crystallises in prisms, m. p. 186°. Only triphenyltriazole and diphenyloxadiazole could be isolated from the product of the action of *s*-acetylphenylhydrazine on dibenzoylhydrazide dichloride.

1-*Methylanilino*-2 : 5-*di*-p-*bromophenyl*-1 : 3 : 4-*triazole*, $C_{21}H_{16}N_4Br_2$, forms small prisms, m. p. 251°.

1-*Anilino*-2 : 5-*diphenyl*-1 : 3 : 4-*triazole methiodide*, $C_{20}H_{16}N_4$,MeI, crystallises in leaflets, m. p. 188°.

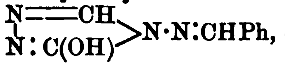
1-*Methylanilino*-2 : 5-*diphenyl*-1 : 3 : 4-*triazole*, $C_{21}H_{18}N_4$, prepared by heating dibenzoylhydrazide dichloride with *as*-phenylmethylhydrazine in benzene solution at 115°, forms small, stout crystals, m. p. 174°.

The author now adopts Busch's formula (Abstr., 1901, i, 488; compare 1906, i, 315) for the benzylidene derivative of Curtius and Heidenreich's dicarbamide (Abstr., 1895, i, 12), as the action of iodine on its silver derivative leads to the formation of the intensely coloured *azo*-compound



$\left.\begin{matrix}\mathrm{N\cdot CO}\\ \|\\ \mathrm{N\cdot CO}\end{matrix}\right>\mathrm{N\cdot N{:}CHPh}$.

Similarly, methenylcarbohydrazide (Curtius and Heidenreich, *loc. cit.*; Busch, *loc. cit.*) must be 1-amino-2-hydroxy-1 : 3 : 4-triazole, since it yields a *benzylidene* derivative,



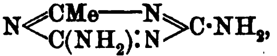
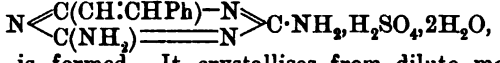
$\left.\begin{matrix}\mathrm{N{=\!=}CH}\\ \mathrm{N{:}C(OH)}\end{matrix}\right>\mathrm{N\cdot N{:}CHPh}$,

crystallising in needles, m. p. 178°.

Purgotti and Viganò's dibenzophenone- and diacetophenone-*p*-urazines (Abstr., 1902, i, 322) are shown to be identical with diphenylketazine (Curtius and Rauterberg, Abstr., 1891, 1359) and bisphenylmethylazimethylene (Curtius and Thun, Abstr., 1891, 1355) respectively.

G. Y.

Condensation of Acetoguanamine with Aromatic Aldehydes. V. Humnicki (*Bull. Acad. Sci. Cracow,* 1907, 16–24).—Formoguanamine (diaminocyanuric dihydride) and its homologues were first prepared by von Nencki (Abstr., 1874, 1089; 1875, 754, 1201; 1876, 188, 191, 509; 1877, i, 299) by the destructive distillation of the corresponding guanidine salt, and the formulæ now assigned to the group are due to Claus (*Ber.*, 1876, 9, 722) and Bamberger and Dieckmann (Abstr., 1892, 736; compare Diels, Abstr., 1899, i, 406).

When acetoguanamine,  $\mathrm{N}{<}\begin{matrix}\mathrm{CMe{-}{-}N}\\ \mathrm{C(NH_2){:}N}\end{matrix}{>}\mathrm{C{\cdot}NH_2}$, is condensed with benzaldehyde in presence of sulphuric acid, *benzylideneacetoguanamine sulphate*,  $\mathrm{N}{<}\begin{matrix}\mathrm{C(CH{:}CHPh){-}N}\\ \mathrm{C(NH_2){=}{=}{=}N}\end{matrix}{>}\mathrm{C{\cdot}NH_2,H_2SO_4,2H_2O}$, m. p. 286° (decomp.), is formed. It crystallises from dilute methyl alcohol in long needles, and on treatment with sodium hydroxide solution yields the *free base*, m. p. 260° (approx.), in small needles. The *hydrochloride*, $C_{11}H_{11}N_5,HCl,H_2O$, is crystalline, as are also the *chromate* and *picrate*. The *dibenzoyl* derivative, m. p. 146°, obtained by heating the base with benzoic anhydride at 130°, crystallises from a mixture of alcohol and benzene, and yields with bromine in chloroform a *bromo*-derivative containing 23·7% of bromine in place of 27·5% as required by the formula $C_{25}H_{19}O_2N_5Br_2$. Benzylideneacetoguanamine is not produced when guanidine cinnamate is submitted to destructive distillation (compare Elzanowski, *Inaug. Diss. Freiburg*, 1898). Formoguanamine does not condense with benzaldehyde in presence of sulphuric acid; acetoguanamine, on the contrary, condenses with a number of aldehydes, but not with acetophenone or benzophenone. With formaldehyde it furnishes a *base* which gives amorphous salts with mineral acids. The *product* contained with *o*-hydroxybenzaldehyde is also amorphous, but that prepared by condensation with *p*-hydroxybenzaldehyde yields a crystalline, yellow *sulphate*. The condensation *product* obtained with *o*-nitrobenzaldehyde also gives a crystalline *sulphate*, but the *substances* obtained from anisole and vanillin are amorphous. The greater reactivity of acetoguanamine appears to be due to the presence of the methyl group, since 2-methylpyridine and 2-methylquinoline show a similar readiness to condense with aldehydes.

Dibenzoylacetoguanamine, m. p. 153—154°, obtained by heating acetoguanamine with benzoic anhydride, crystallises from alcohol or benzene in needles. *Dibenzoylformoguanamine*, m. p. 207—208°, similarly prepared, crystallises in broad needles from the same solvents.

T. A. H.

Xanthine Bases. Ernst Salkowski (*Biochem. Zeitsch.*, 1907, **4**, 244—247).—Polemical. Certain statements in Steudel's recent historical article on the subject (*Biochem. Zentr.*, **6**, 125) are objected to.

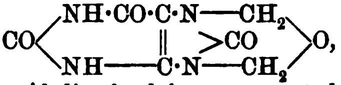
W. D. H.

Compounds of Uric Acid with Formaldehyde. Arthur Nicolaier (*Chem. Zentr.*, 1907, i, 949; from *Arch. klin. Med.*, **89**, 168—185. Compare Abstr., 1905, ii, 188).—The solvent action of formaldehyde on uric acid results from the formation of *additive* compounds which have been found in urotropin urine.

Diformaldehyde-uric acid (Weber, Pott, and Tollens, Abstr., 1898, i, 66; Weber and Tollens, *ibid.*, 300) is decomposed by alkalis, but is stable towards acids, gives the murexide reaction, reduces silver nitrate in alkaline solution, and forms a *compound* with 2 mols. of urotropin. His statement that diformaldehyde-uric acid may be separated from uric acid by means of concentrated sulphuric acid could not be confirmed.

Formaldehyde-uric acid (*oxymethylene-uric acid*), $C_5H_4O_3N_4,CH_2O$, crystallises in needles or prisms, decomposes slowly at 37°, rapidly above 320° or when treated with alkalis, and gives reactions similar to those of the diformaldehyde-uric acid; it forms crystalline *alkali* salts.

Anhydroformaldehyde-uric acid,



formed by pouring diformaldehyde-uric acid dissolved in concentrated sulphuric acid into ice-water, or by the action of trioxymethylene on uric acid in sulphuric acid solution, decomposes at 125° or on prolonged boiling with water, is soluble in alkalis, reduces silver nitrate, and gives an orange coloration when evaporated with nitric acid and treated with ammonia. It is not found in urine, being decomposed in the body.

The author considers that the formation of the additive compounds prevents the total decomposition of uric acid in the human body.

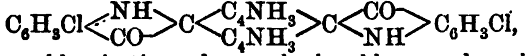
G. Y.

Indigotin-like Groups of Blue Colouring Matters from Isatin.

Carl Liebermann and **Rudolph Krauss** (*Ber.*, 1907, 40, 2492—2515).—The authors have prepared, in the pure state, a number of members of the pyrrole-blue group (compare Liebermann and Häse, Abstr., 1905, i, 841), and have also extended Schotten's isatin-blue group (Abstr., 1891, 928, 1491). Attempts to obtain useful variants of these colouring matters by modifying the basic portion of the molecule have been successful in only one instance, in which piperazine was introduced in place of the piperidine.

In the pyrrole-blue group the authors have prepared several new derivatives. To the two pyrrole-blues, A and B, the new formulæ, $C_{24}H_{16}O_3N_4$ and $C_{24}H_{16}O_2N_4$ respectively, are ascribed (compare Liebermann and Häse, *loc. cit.*). The A-compound is formed by the action of the oxygen of the air on the B-derivative, which passes into the other the more readily as the conditions of its preparation are rendered more unfavourable. The formation of compounds of the B-type, such as dichloropyrrole-blue B, is regarded as taking place according to the equation: $2C_8H_4O_2NCl + 2C_4H_5N = 2H_2O + C_{24}H_{14}O_2N_4Cl_2$, and the conclusion is drawn that compounds of the pyrrole-blue group have the same structure as those of the indophenines (compare Baeyer and Lazarus, Abstr., 1886, 154; Oster, Abstr., 1904, i, 914).

Dichloropyrrole-blue B,



$$C_6H_3Cl<\begin{matrix}NH\\CO\end{matrix}>C<\begin{matrix}C_4NH_3\\C_4NH_3\end{matrix}>C<\begin{matrix}CO\\NH\end{matrix}>C_6H_3Cl,$$

obtained from chloroisatin and pyrrole, is a blue powder with metallic lustre and closely resembles pyrrole-blue B. The *chloroisatin*,

$$C_8H_4O_2NCl,$$

here used is obtained by passing chlorine into water containing finely-divided isatin in suspension, and separates from alcohol in crystals, m. p. 246°.

Tetrachloropyrrole-blue, prepared from dichloroisatin, was not analysed.

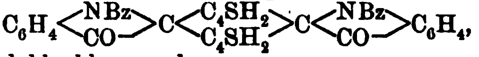
Dibromopyrrole-blue A, $C_{24}H_{14}O_8N_4Br_2$, obtained from bromoisatin and pyrrole, separates from alcohol in crystals, m. p. 255°.

Tetrabromopyrrole-blue A or B, $C_{24}H_{12}O_8N_4Br_4$ or $C_{24}H_{12}O_2N_4Br_4$, prepared from dibromoisatin, forms a blue powder with slight metallic lustre.

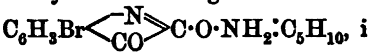
Dinitropyrrole-blue A, $C_{24}H_{14}O_8N_4(NO_2)_2$, obtained from nitroisatin and pyrrole, exhibits metallic lustre. The *nitroisatin*, $C_8H_4O_4N_2$, employed crystallises from alcohol in yellow needles, m. p. 245° (decomp.).

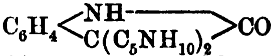
Acetyl-ψ-isatin and pyrrole yield pyrrole-blue B, the acetyl group being removed during the reaction.

Dibenzoylpyrrole-blue A, $C_{24}H_{14}O_8N_4Bz_2$, and B, $C_{24}H_{14}O_2N_4Bz_2$, prepared from benzoyl-ψ-isatin, form blue powders, the B-compound being less soluble than the A and exhibiting metallic lustre. The B-compound dissolves in cold concentrated sulphuric acid without change, but after some time the solution is found to contain benzoic and *pyrrole-blue-disulphonic acids*, $C_{24}H_{14}O_2N_4(SO_3H)_2$.

Benzoylisatin exhibits the indophenine reaction, *dibenzoylisatinindophenine*,  $C_6H_4{<}\substack{NBz\\CO}{>}C{<}\substack{C_4SH_2\\C_4SH_2}{>}C{<}\substack{NBz\\CO}{>}C_6H_4$, being obtained as an insoluble, blue powder.

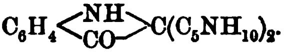
If indole or acetonylpyrrole is used in place of pyrrole, steric relations prevent the formation of compounds analogous with pyrrole-blue.

The authors confirm the formulæ given by Schotten (*loc. cit.*) for the colourless dipiperides prepared from isatin and bromoisatin, and also the provisional formula, $C_{21}H_{17}O_2N_3$, given by him to isatin-blue. Substituted isatins vary in their capability of yielding monopiperides, which are readily obtained when the acid character of the isatin is reinforced by the introduction of a halogen or acid group. All the six monopiperides prepared (*vide infra*) resemble one another closely in external appearance, dissolve readily in alcohol, and form measurable, honey-yellow prisms. Whether formulæ analogous to that chosen by Schotten (*loc. cit.*) for the dibromoisatin derivative are to be ascribed to them, or whether they are to be regarded as salts of normal isatin, for example,  $C_6H_3Br{<}\substack{N\\CO}{>}C\cdot O\cdot NH_2{:}C_5H_{10}$, is uncertain. In the cold, acids decompose them into their components far more slowly than is the case with true salts, but this may result from the peculiar character of normal isatin salts. The dipiperides form white leaflets sparingly soluble in alcohol, and yield insoluble blue colouring matters when treated with dehydrating agents such as acetic anhydride. They are, like the monopiperides, unstable compounds, being rapidly resolved into their components by cold mineral acids, and have the formula:



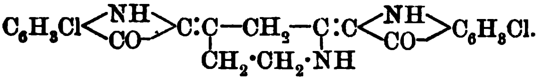
$$C_6H_4{<}\substack{NH\text{———}\\C(C_5NH_{10})_2}{>}CO$$

or



$$C_6H_4{<}\substack{NH\\CO}{>}C(C_5NH_{10})_2.$$

Isatin-blue may be readily purified by dissolving in fuming hydrochloric acid, diluting with water, filtering, and treating with ammonia. The annexed structure given to isatindipiperide-blue, indicates that the two isatin residues are united by a double linking, just as in indigo, except that in the present instance the union takes place by way of the piperidine residue.



Isatinmonopiperide, $C_6H_4{<}\substack{N\\CO}{>}C\cdot O\cdot NH_2{:}C_5H_{10}$, or

$$C_6H_4{<}\substack{NH_2\\CO}{>}CO\cdot N{:}C_5H_{10},$$

crystallises from alcohol in yellow, monoclinic prisms [A. Fock. $a:b:c = 1\cdot1027:1:0\cdot5044$; $\beta = 93°51'$], m. p. 135°, yields no colour when heated with acetic anhydride, and is quantitatively decomposed into its constituents by fuming hydrochloric acid. *Bromoisatinmonopiperide*, $C_8H_4O_2NBr,C_5H_{11}N$, separates in yellow prisms, m. p. 208°. Dibromoisatinmonopiperide (compare Schotten, *loc. cit.*) forms monoclinic crystals [A. Fock. $a:b:c = 1\cdot2349:1:0\cdot7575$; $\beta = 99°2'$]. *Chloroisatinmonopiperide*, $C_8H_4O_2NCl,C_5H_{11}N$, has m. p. 185°. *Nitroisatinmonopiperide*, $C_8H_4O_2N\cdot NO_2,C_5H_{11}N$, separates in pale yellow leaflets, m. p. 198°. *Benzoylisatinmonopiperide*, $C_8H_4O_2NBz,C_5H_{11}N$, crystallises from light petroleum in leaflets, m. p. 138—140°.

Isatinpiperazide, $C_{24}H_{28}O_8N_6$, decomposes at about 196°, and appears to be a compound intermediate between the mono- and di-piperides. It gives a small proportion of a blue colouring matter on treatment with acetic anhydride.

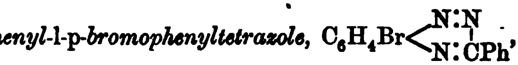
Dibromoisatinpiperazide, $C_4H_8({:}NH_2\cdot C_8H_2Br_2\cdot NO_2)_2$, or bis-*dibromoisatinic piperazide*, $C_4H_8({:}N\cdot CO\cdot CO\cdot C_6H_2Br_2\cdot NH_2)_2$, prepared from dibromoisatin and piperazine, is a yellow compound decomposing at 245°.

The isatinpiperide-blues described below were prepared by the action of acetic anhydride on the corresponding dipiperides suspended in boiling toluene.

Isatinpiperide-blue and dibromoisatinpiperide-blue were obtained purer than the preparations of Schotten (*loc. cit.*). Isatinpiperide-blue hydrochloride and *dichloroisatinpiperide-blue*, $C_{21}H_{15}O_2N_3Cl_2$, were also prepared.
T. H. P.

Synthesis of Tetrazoles from Phenylazoimide. Otto Dimroth and Siegfried Merzbacher (*Ber.*, 1907, 40, 2402—2404. Compare Abstr., 1905, i, 98; this vol., i, 97).—When heated in alcoholic sodium ethoxide solution in a sealed tube in the water bath, phenylazoimide and benzylidenephenylhydrazone react forming aniline and 1:4-diphenyltetrazole. Since under similar conditions, phenylazoimide and benzylidene-*p*-bromophenylhydrazone form aniline and 4-*phenyl*-1-p-*bromophenyltetrazole*, the group NPh appearing as aniline must be that of the phenylazoimide.

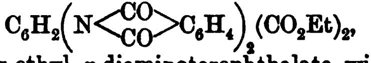
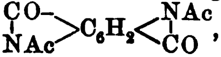
1:4-Diphenyltetrazole has m. p. 101·5—102°, at which temperature Wedekind's preparation (m. p. 106—107°: Abstr., 1896, i, 630) is now found to melt.

4-*Phenyl*-1-p-*bromophenyltetrazole*,  $C_6H_4Br<\begin{matrix}N:N\\N:CPh\end{matrix}$, crystallises in slightly yellow prisms, m. p. 122°. G. Y.

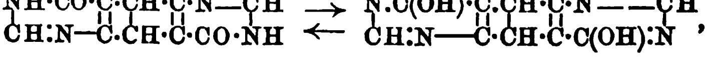
Quinazolines. XIX. Synthesis of 1:3:6:8-Naphthatetrazines from p-Diaminoterephthalic Acid and from Certain of its Derivatives. MARSTON T. BOGERT and JOHN MAURICE NELSON (*J. Amer. Chem. Soc.*, 1907, **29**, 729—739).—Naphthatetrazines have been prepared by Bogert and Dox (Abstr., 1905, i, 841, 949) by the condensation of ethyl succinylsuccinate with guanidine and with acetamidine. Similar compounds have now been obtained by heating ethyl *p*-diaminoterephthalate with formamide, by heating its diacetyl derivative with primary amines, by the action of primary amines on the dilactam of *s*-2 : 5-diacetylaminoterephthalic acid, and by heating ethyl diphenylcarbaminoterephthalate with aniline. With the exception of 4 : 9-diketo-2 : 7-dimethyl-3 : 8-di*iso*amyltetrahydro-1 : 3 : 6 : 8-naphthatetrazine, all the naphthatetrazines thus prepared either have very high m. p.'s or are infusible, and are insoluble or nearly so in the usual organic solvents. Those compounds which contain the group $\cdot CO\cdot NH\cdot \rightleftarrows \cdot C(OH):N\cdot$ dissolve readily in dilute alkali hydroxides and are reprecipitated by dilute acids.

Ethyl 2 : 5-*diphenylcarbaminoterephthalate*,

$$C_6H_2(NH\cdot CO\cdot NHPh)_2(CO_2Et)_2,$$

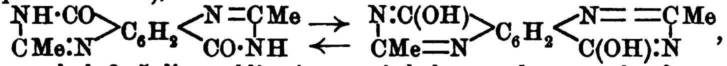
m. p. 262° (decomp.), obtained by treating ethyl *p*-diaminoterephthalate with phenylcarbimide, forms light yellow crystals. When this substance is heated with hydrazine hydrate in a sealed tube at 130°, a yellow, amorphous *substance* is produced which does not melt below 320°. *Ethyl* 2 : 5-*tetra-acetyldiaminoterephthalate*, $C_6H_2(NAc_2)_2(CO_2Et)_2$, m. p. 207—208° (corr.), from the action of acetic anhydride on ethyl diphenylcarbaminoterephthalate, forms colourless crystals. *Ethyl* s-2 : 5-*diacetyldiaminoterephthalate*, $C_6H_2(NHAc)_2(CO_2Et)_2$, m. p. 219° (corr.), forms yellowish-white crystals with a green fluorescence, and when heated with propylenediamine at 150° in a sealed tube yields a *substance* which separates in large yellow crystals. *Ethyl* 2 : 5-*diphthaliminoterephthalate*,  $C_6H_2\left(N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4\right)_2(CO_2Et)_2$, m. p. 326° (corr.), obtained by fusing ethyl *p*-diaminoterephthalate with phthalic anhydride, forms cream-coloured crystals. When this substance is treated with ammonia at 150° in a sealed tube, a product is obtained which on heating yields a white, crystalline *sublimate*, m. p. 228° (uncorr.). If an alcoholic solution of ethyl 2 : 5-diacetyldiaminoterephthalate is treated with sodium amalgam, a product is obtained which on boiling with acetic anhydride yields the *dilactam*,  $\begin{matrix}CO-\\NAc\end{matrix}>C_6H_2<\begin{matrix}NAc\\CO\end{matrix}$, which separates as white, infusible flakes. Bogert and Dox (Abstr., 1905, i, 841) have stated that *p*-diaminoterephthalic acid is not changed by boiling acetic anhydride, but it is now found that the above dilactam is produced.

4 : 9-*Diketotetrahydro*-1 : 3 : 6 : 8-*naphthatetrazine* (4 : 9-*dihydroxy*-1 : 3 : 6 : 8-*naphthatetrazine*),



$$\begin{matrix}NH\cdot CO\cdot C\cdot CH\cdot C\cdot N{=}CH\\CH:N-C\cdot CH\cdot C\cdot CO\cdot NH\end{matrix}\rightleftarrows\begin{matrix}N:C(OH)\cdot C.CH\cdot C\cdot N{=}CH\\CH:N-C\cdot CH\cdot C\cdot C(OH):N\end{matrix},$$

is obtained from ethyl *p*-diaminoterephthalate and formamide as a pale yellow, amorphous powder. 4 : 9-*Diketo*-2 : 7-*dimethyltetrahydro*-1 : 3 : 6 : 8-*naphthatetrazine* (4 : 9-*dihydroxy*-2 : 7-*dimethyl*-1 : 3 : 6 : 8-*naphthatetrazine*),

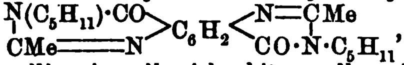


$$\begin{array}{l}NH\cdot CO\\ CMe{:}N\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}N{=}CMe\\ CO\cdot NH\end{array} \rightleftarrows \begin{array}{l}N{:}C(OH)\\ CMe{=}N\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}N{=}{=}CMe\\ C(OH){:}N\end{array},$$

from ethyl 2 : 5-diacetyldiaminoterephthalate and ammonia, forms a pale yellow, amorphous powder.

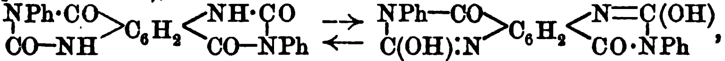
2 : 5-*Diacetyldiaminoterephthal*iso*amylamide*,

$$C_6H_2(NHAc)_2(CO\cdot NH\cdot C_5H_{11})_2,$$

m. p. 255° (corr.), obtained by heating ethyl 2 : 5-diacetyldiaminoterephthalate or the dilactam with *iso*amylamine, forms long, silky needles, and when boiled with dilute potassium hydroxide is converted into 4 : 9-*diketo*-2 : 7-*dimethyl*-3 : 8-*di*iso*amyltetrahydro*-1 : 3 : 6 : 8-*naphthatetrazine*,  $\begin{array}{l}N(C_5H_{11})\cdot CO\\ CMe{=\!=}N\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}N{=}CMe\\ CO\cdot N\cdot C_5H_{11}\end{array}$, m. p. 179° (corr.), which crystallises in yellowish-white needles with a green fluorescence, and yields a yellowish-white, crystalline *bromo*-derivative, m. p. about 290°.

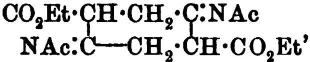
4 : 9-*Diketo*-3 : 8-*diphenyl*-2 : 7-*dimethyltetrahydro*-1 : 3 : 6 : 8-*naphthatetrazine*, from the dilactam of 2 : 5-diacetyldiaminoterephthalic acid and aniline, crystallises in pale, greenish-yellow leaflets.

2 : 4 : 7 : 9-*Tetraketo*-3 : 8-*diphenyloctahydro*-1 : 3 : 6 : 8-*naphthatetrazine* (2 : 7-*dihydroxy*-4 : 9-*diketo*-3 : 8-*diphenyltetrahydro*-1 : 3 : 6 : 8-*naphthatetrazine*),



$$\begin{array}{l}NPh\cdot CO\\ CO{-}NH\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}NH\cdot CO\\ CO{-}NPh\end{array} \rightleftarrows \begin{array}{l}NPh{-}CO\\ C(OH){:}N\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}N{=}C(OH)\\ CO\cdot NPh\end{array},$$

from ethyl 2 : 5-diphenylcarbaminoterephthalate and aniline, forms bright yellow crystals.

Ethyl diacetyliminosuccinylsuccinate,  $\begin{array}{l}CO_2Et\cdot CH\cdot CH_2\cdot C{:}NAc\\ NAc{:}C{-\!-}CH_2\cdot CH\cdot CO_2Et\end{array}$, m. p. 215—216° (corr.), obtained by the action of acetic anhydride on ethyl di-iminosuccinylsuccinate, forms white crystals with a green fluorescence; the free *acid* is very unstable. *Ethyl dibenzoyliminosuccinylsuccinate*, m. p. 255° (uncorr.), forms yellow, feathery needles, and when heated with a solution of bromine in acetic anhydride is converted into a *substance*, m. p. 264° (uncorr.), which is probably ethyl dibenzoylaminoterephthalate. E. G.

Action of Nitrites and Nitrosyl Chloride on Aldazines. HARTWIG FRANZEN and F. ZIMMERMANN (*Ber.*, 1907, 40, 2009—2012).—Benzylidineazine may be boiled with amyl nitrite without action occurring; if, however, a drop or two of acetyl chloride is added to an ethereal solution of the azine and nitrite, a reaction at once takes place, gas is evolved, consisting of nitrogen and nitrous oxide in equal volumes, and benzaldehyde and benzylidine di*iso*amyl ether are formed. The corresponding diethyl compound is obtained when ethyl nitrite is employed. This reaction also occurs when substituted benzylidineazines are used, thus cuminaldehyde and iso*propylbenzylidenedi*iso*amyl ether*,

$C_{20}H_{24}O_2$, are obtained from *iso*propylbenzylidineazine. Experiments, however, with salicylaldazine and *o*-methoxybenzylidineazine were without result.

Nitrosyl chloride (2 mols.) and benzylidineazine (1 mol.) in ether give benzylidene chloride (1 mol.), benzaldehyde (1 mol.), nitrogen (1 mol.), and nitrous oxide (1 mol.).

This result is used to explain the action of the acetyl chloride in the above experiments. The nitrosyl chloride, resulting from the interaction of nitrite and chloride, gives benzylidene chloride, which, in its turn, reacts with free amyl alcohol to produce the acetal compound and hydrogen chloride. The trace of hydrogen chloride regenerates nitrosyl chloride with the nitrite, and so the cycle of changes is repeated until the action is completed. W. R.

Behaviour of Diazo-compounds with Keto-enolic Desmotropic Compounds. OTTO DIMROTH (*Ber.*, 1907, 40, 2404—2411).—5-Hydroxy-1-phenyl-1 : 2 : 3-triazole couples with diazobenzene chloride forming two isomeric products (Dimroth and Eberhardt, Abstr., 1905, i, 100), of which the scarlet isomeride must be an azo-derivative. With the object of throwing light on the constitution of the colourless isomeride, the action of diazobenzene chloride and of nitrous acid on the desmotropic compounds, 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid and 1-phenyl-1 : 2 : 3-triazole-5-one-4-carboxylic acid, has been investigated. It is found that whilst the enolic acid loses carbon dioxide and forms the scarlet azo-compound and 4-*iso*nitroso-1-phenyl-5-triazolone (this vol., i, 96) respectively, the keto-acid does not react with either reagent. These results led the author to study the action of diazo-compounds on the enolic and keto-forms of other desmotropic compounds.

The manner in which the coupling of enolic and keto-compounds with diazo-compounds may take place is discussed, and a number of experiments described, the compounds selected for study being such as permit of the isolation of both forms, the intramolecular transformation taking place in solution only slowly. To avoid this transformation during the reaction, the coupling was carried out with *p*-nitro*anti*diazobenzene hydrate in alcoholic solution at temperatures below 0°. It is found that the reaction takes place readily with the enolic compounds, but that in no case does the keto-form couple (compare Hantzsch and Kissel, Abstr., 1900, i, 89; Hantzsch, *ibid.*, 618). Also the keto-form of tribenzoylmethane, the enolic modification of which is unstable in alcoholic solution, does not react with *p*-nitro*anti*diazobenzene hydrate.

Contrary to Bülow and Schlesinger's view (Abstr., 1900, i, 56), ethyl benzeneazodiacetylsuccinate must be formed by the action of diazobenzene chloride on the enolic form of the ester, resulting from transformation of the diketo-modification in presence of sodium acetate, and must have the constitution

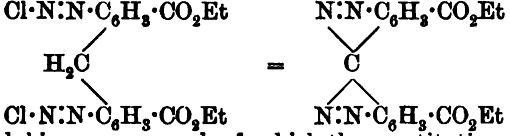
$$CO_2Et\cdot CHAc\cdot CAc(CO_2Et)\cdot N_2Ph,$$

since, if an enolic compound as considered by these authors, it must couple with a second molecule of diazobenzene chloride.

Ethyl p-*nitrobenzeneazomesityloxidoxalate*, $C_{16}H_{17}O_6N_3$, crystallises from alcohol in orange prisms, m. p. 134°. p-*Nitrobenzeneazoacetyldibenzoylmethane*, $C_{23}H_{17}O_5N_3$, crystallises in orange needles, m. p. 110·5°, and when crystallised from boiling alcohol is converted into a colourless *isomeride*, m. p. 201°; both isomerides are hydrolysed by sodium ethoxide or ammonia, forming p-*nitrobenzeneazodibenzoylmethane*, $C_{21}H_{15}O_4N_3$, which crystallises in yellow leaflets, m. p. 173°.

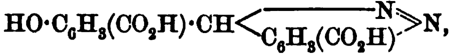
Ethyl p-*nitrobenzeneazodiacetylsuccinate*, $C_{18}H_{21}O_8N_3$, forms yellow crystals, m. p. 153°. G. Y.

A New Type of Bisazo-compounds. Henri Duval (*Compt. rend.*, 1907, **144**, 1222—1224).—When ethyl diaminodiphenylmethanedicarboxylate is diazotised in strongly acid solution at a low temperature, it undergoes the normal reaction, but if the temperature is raised or insufficient acid is present, the bisdiazo-compound reacts thus:

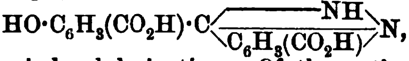


+ 2HCl, forming a mixed bisazo-compound, of which the constitution is determined by its method of preparation, properties, and analysis. By heating with sulphuric acid, one of the azo-groups is replaced by hydroxyl, whilst the other is unattacked.

The product may be represented by one of two formulæ:

(I) 

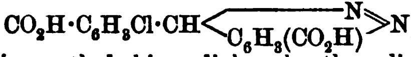
$HO\cdot C_6H_3(CO_2H)\cdot CH{<}\begin{matrix}\text{——————}N\\ C_6H_3(CO_2H)\end{matrix}{>}N$,

(II) 

$HO\cdot C_6H_3(CO_2H)\cdot C{\Large\langle}\begin{matrix}\text{——————}NH\\ C_6H_3(CO_2H)\end{matrix}{\Large\rangle}N$,

as (I) an azo-derivative; (II) an indazyl derivative. Of these, the former is probably correct, since the compound is insoluble in acids, forms only a monosubstituted *O*-acetyl derivative, is not attacked by ethyl iodide, and is reduced by sodium amalgam to a hydrazo-compound, which is reoxidised by mercuric oxide to the original substance.

Ethyl bisazodiphenylmethanedicarboxylate forms yellow needles, m. p. 280° (decomp.), which are reduced by stannous chloride to a colourless hydrazo-compound, the latter being reoxidised by mercuric oxide in alkaline solution to the original substance. *Hydroxyazodiphenylmethanedicarboxylic acid* (I above) forms clear yellow needles which are easily esterified by ethyl alcohol and hydrochloric acid. The *ethyl ester* crystallises in needles, m. p. 204°, which give a blue coloration with ferric chloride, and which dissolve in alkali hydroxides, but are reprecipitated by carbon dioxide. This ester, when treated with acetic anhydride, gives an *acetyl* derivative, m. p. 218°, which gives no coloration with ferric chloride. *Ethyl chloroazodiphenylmethanedicarboxylate*,



$CO_2H\cdot C_6H_3Cl\cdot CH{<}\begin{matrix}\text{——————}N\\ C_6H_3(CO_2H)\end{matrix}{>}N$, m. p. 151°, is formed by heating ethyl bisazodiphenylmethanedicarboxylate with hydrochloric acid in a sealed tube at 150°. E. H.

Phenol-2 : 4 : 6-trisazobenzene. EUGÈNE GRANDMOUGIN and H. FREIMANN (*Ber.*, 1907, 40, 2662—2664).—Phenol-2 : 4 : 6-trisazobenzene, $C_6H_2(N{:}NPh)_3{\cdot}OH$, is formed when 3 mols. of diazobenzene chloride react with phenol in alkaline solution. It is freed from the accompanying bisazobenzene by extraction with alcohol, and crystallises from nitrobenzene in slender, orange needles, m. p. 215°. It dissolves in sodium ethoxide solution with a red coloration, and with sulphuric acid, it gives a deep reddish-violet colour. On reduction it yields 2 : 4 : 6-triaminophenol; this result fixes the position of the azo-groupings. The *acetate* forms yellow crystals, m. p. 165°.

W. R.

Tautomerism of Diazoamino-compounds. OTTO DIMROTH, M. EBLE, and W. GRUHL (*Ber.*, 1907, 40, 2390—2401. Compare Abstr., 1905, i, 311).—The behaviour of phenylmethyltriazen, on the one hand, with phenylcarbimide and, on the other, with acids, led to the assumption that the substance exists in the tautomeric forms: (I) $NPh{:}N{\cdot}NHMe$ and (II) $NHPh{\cdot}N{:}NMe$. As a proof of (II) by the action of acids was indirect, it seemed desirable to seek for a reaction leading to the formation of derivatives of the type $NPhR{\cdot}N{:}NMe$. With this object, the formation of bisdiazoamino-compounds has been investigated.

Phenylmethyltriazen couples with diazobenzene salts forming bisbenzeneazomethylamine, prepared previously by Goldschmidt and Badl (Abstr., 1889, 774) and considered by these authors to have the constitution $NMe(N_2Ph)_2$, since when boiled with dilute sulphuric acid it yields methylamine, aniline, methyl alcohol, phenol, and aminoazobenzene. It having been found now that the action of alcoholic sulphuric or hydrochloric acid on the bisdiazoamino-compound at temperatures below 0° leads to the formation of 1 mol. of nitrogen and 1 mol. of the diazobenzene salt, isolated in the form of benzeneazo-β-naphthol, it seemed probable that the bisdiazoamino-compound has the unsymmetrical constitution: $N_2Ph{\cdot}NPh{\cdot}N_2Me$. Were this the case, the product obtained by coupling phenylmethyltriazen with p-diazotoluene chloride must be isomeric with that obtained from *p*-tolylmethyltriazen and diazobenzene chloride. It is shown that, on the contrary, the products of every such pair of reactions investigated are identical in all respects, hence the bisdiazoamino-compounds must have the constitution $N_2R{\cdot}NR'{\cdot}N_2R''$. It is argued that the decomposition of the bisdiazoamino-compounds must take place in two stages, the products of the first stage being the arylmethyltriazen and the diazochloride, and that phenylmethyltriazen exists only in the form (I), and is not tautomeric. The decomposition of arylmethyltriazens by acids is discussed, and the formation of intermediate additive products, $NHR{\cdot}NCl{\cdot}NHMe$ or $NHR{\cdot}N{:}NHMeCl$, postulated.

Attempts to prepare isomeric triazens by the action of magnesium p-tolyl bromide on phenylazoimide and by that of magnesium phenyl bromide on p-tolylazoimide were unsuccessful, the products of the two reactions being identical, as were also those of other similar pairs of reactions. *Phenyl*-p-*phenetyltriazen* has the constitution

$$N_2Ph{\cdot}NH{\cdot}C_6H_4{\cdot}OEt,$$

since with phenylcarbimide it forms a *phenylcarbamido*-derivative, which on hydrolysis yields diazobenzene chloride and *phenyl*-p-*phenetylcarbamide*. For similar reasons, *phenyl-a-naphthyltriazen* must have the constitution $C_{10}H_7 \cdot N_2 \cdot NHPh$. In agreement with these constitutions, the triazens when decomposed by means of cold dilute hydrochloric acid, yield diazobenzene chloride and *p*-phenetidine, and *a*-diazonaphthalene chloride and aniline respectively. On the other hand, the decomposition by means of boiling dilute hydrochloric acid is more complicated, phenyl-α-naphthyltriazen yielding aniline, *a*-napthylamine, phenol, *a*-naphthol, and benzeneazonaphthylamine. It is considered that this results from the interchange,

$$N_2RCl + NH_2R' = NH_2R + N_2R'Cl$$

(compare Griess, Abstr., 1883, 56; Schraube and Fritsch, Abstr., 1896, i, 221; Hantzsch and Perkin, Abstr., 1897, i, 465), which takes place in acid solution slowly at the ordinary temperature and therefore presumably more rapidly in the boiling acid. To this interchange must be ascribed also the complicated decomposition of diazoamino-compounds observed by Noelting and Binder (Abstr., 1888, 271).

The following arylmethyltriazens, $N_2R \cdot NHMe$, are formed by the action of magnesium methyl iodide on the corresponding diazo-imides.

$R = C_7H_7(p)$: crystallises from light petroleum in colourless plates, m. p. 81·5°; the *silver* derivative was analysed. $R = C_6H_4Br(p)$: crystals, m. p. 86—86·5°. $R = C_6H_4 \cdot OEt(p)$: m. p. 73°.

The bisarylazomethylamines, $N_2R \cdot NMe \cdot N_2R'$, were hydrolysed with cold alcoholic hydrogen chloride.

$R = Ph$, $R' = C_7H_7(p)$: yellow needles, m. p. 84·5 or, in one preparation, m. p. 76°, yields *p*-diazotoluene chloride and aniline. $R = Ph$, $R' = C_6H_4Br(p)$: brownish-yellow needles, m. p. 119°, yields diazobenzene chloride and *p*-bromoaniline. $R = Ph$, $R' = C_6H_4 \cdot OEt(p)$: brownish-yellow prisms, m. p. 71·5°, yields diazobenzene chloride and *p*-phenetidine. The diazo-chlorides were isolated by coupling with *β*-naphthol, the amines by conversion into the acetyl derivatives.

Phenyl-p-*phenetyltriazen*, $C_{14}H_{15}ON_3$, crystallises in yellow leaflets, m. p. 113°. s-*Phenyl*-p-*phenetylcarbamidoazobenzene*,

$$NHPh \cdot CO \cdot N(C_6H_4 \cdot OEt) \cdot N_2Ph,$$

forms yellowish-white needles, m. p. 115°. s-*Phenyl*-p-*phenetylcarbamide*, $NHPh \cdot CO \cdot NH \cdot C_6H_4 \cdot OEt$, m. p. 187°, crystallises from alcohol.

Phenyl-*a*-naphthyltriazen crystallises in reddish-brown needles, m. p. 84°. s-*Diphenylcarbamidoazonaphthalene*,

$$NHPh \cdot CO \cdot NPh \cdot N_2 \cdot C_{10}H_7,$$

crystallises in yellow needles, m. p. 110°. G. Y.

Synthesis of Protein by Trypsin. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1907, **3**, 87—94).—The amino-acids resulting from the hydrolysis of protamine (derived from *Roccus lineatus*) by trypsin, were placed in concentrated form either as the free acids or their carbonates in contact with a very resistant trypsin prepared from the mollusc, *Schizothærus nuttallii*, for five months at room temperature. At the end of this time, 1·8 grams of protamine were obtained, 400 grams of protamine sulphate having been originally employed for the hydrolysis. . A blank experiment in which the trypsin solution had been boiled gave negative results. The term synthesis through ferment action is in the direct sense a misnomer. The ferment simply accelerates the reaction of synthesis, but even in the presence of the ferment the velocity is slow. W. D. H.

Synthesis of Protein by Pepsin. T. Brailsford Robertson (*J. Biol. Chem.*, 1907, **3**, 95—99).—Paranuclein, which is derived from caseinogen by incomplete digestion with pepsin, is probably a mixture of two substances differing in their percentage of phosphorus. Paranuclein containing 4·175% of phosphoric acid digested with lime-water at 40° for twelve hours yields a small quantity of paranuclein *A*, which contains only 1·5% of phosphoric acid. By acting at 40° on an acid concentrated solution of the products of the peptic digestion of caseinogen, containing no caseinogen or paranuclein, a substance is precipitated which is identical with paranuclein *A*. Appropriate control experiments gave negative results. W. D. H.

Hydrolysis of Excelsin. Thomas B. Osborne and Samuel H. Clapp (*Amer. J. Physiol.*, 1907, **19**, 53—60).—Excelsin (the globulin of Brazil nuts) was obtained in crystalline form: hexagonal plates belonging to the regular system. On acid-hydrolysis it yielded in parts per cent.: glycine, 0·60; alanine, 2·33; aminovaleric acid, 1·51; leucine, 8·7; proline, 3·65; phenylalanine, 3·55; aspartic acid, 3·85; glutamic acid, 12·94; serine, 0; cystine, 0; oxyproline, 0; tyrosine, 3·03; arginine, 16·02; histidine, 1·47; lysine, 1·64; ammonia, 1·8. The large proportion of arginine is unusual; tryptophan was present. W. D. H.

Hydrolysis of Hordein. Thomas B. Osborne and Samuel H. Clapp (*Amer. J. Physiol.*, 1907, **19**, 117—124).—The composition of hordein, the alcohol-soluble protein of barley, is, C, 54·29; H, 6·80; N, 17·21; S, 0·83, and O, 20·87%. On acid-hydrolysis it yields: glycine, 0; alanine, 0·43; valine, 0·13; leucine, 5·67; proline, 13·73; phenylalanine, 5·03; glutamic acid, 36·35; tyrosine, 1·67; arginine, 2·16; histidine, 1·18; lysine, 0; ammonia, 4·87. Aspartic acid and serine were not isolated; cystine and oxyproline were not determined, and tryptophan was found to be present. Like other proteins soluble in alcohol, it yields no lysine, little histidine and arginine, and much ammonia. The proportion of glutamic acid is the same as in gliadin. Proline, however, is twice as abundant as in gliadin, and greatly exceeds that obtained so far from any protein. W. D. H.

The Existence in Wool of Sulphur united with Oxygen. Paul N. Raikow (*Chem. Zeit.*, 1907, **31**, 539—540. Compare Abstr., 1905, i, 725).—Polemical. A reply to Grandmougin (*Chem. Zeit.*, 1907, **31**, 174). P. H.

The Lecithin of Bone-Marrow. S. W. Otolski (*Biochem. Zeitsch.*, 1907, **4**, 124—153).—The lecithin found in bone-marrow yields on decomposition: choline, glycero-phosphoric acid, and unsaturated fatty-acids. It is best prepared by extraction with warm 96% alcohol; this is treated with ether and the precipitated substance separated by decantation; the ether-alcohol solution is then evaporated to dryness, the residue dissolved in ether, and the lecithin precipitated from the ethereal solution by acetone. Bergell's method is not advisable. The lecithin is best estimated by cadmium determinations in the cadmium lecithinate. W. D. H.

The Solubility of Albumoses and Ferments with Reference to their Relationships to Lecithin and Mastic. LEONOR MICHAELIS and PETER RÓNA (*Biochem. Zeitsch.*, 1907, 4, 11—20).—The authors' researches bear on the question of the nature of toxin-lecithide and the chemistry of toxin action. Attention is called to the great biological significance of the discovery that certain protein colloidal substances, although themselves soluble in water only, dissolve in such organic solvents as chloroform if lecithin is dissolved therein at the same time. The question at once arises as to whether these phenomena are due to the specific chemical nature of lecithin, or whether they represent the mutual adsorption of two colloidal substances. The experiments described support the latter view. Mastic, a substance in no way connected with lecithin in its chemical nature, shows a marked similarity to it in its physical properties. The authors find also that its solubility-relationships with reference to albumoses and ferments are almost a strict counterpart of those of lecithin.

The Behaviour of Albumoses.—When a suspension of mastic is precipitated by acidification in the presence of Riedel's peptone, the percentage of the total nitrogen which comes down is independent of the original concentration of the peptone and probably represents that portion of the peptone which is of a colloidal nature. When the precipitate, washed with water until no further biuret reaction is given, is dried, it may be dissolved almost completely in chloroform or alcohol. On adding ether, a precipitation occurs. This precipitate is also a peptone-mastic combination. It differs, however, from the former one in that the proportion of mastic is smaller, and that, when treated with water, the peptone tends to dissolve out. With lecithin, almost precisely similar phenomena were observed. The following conclusions were arrived at from further experiments on these lines: the difference of solubility in various solvents do not appear to be so well marked with lecithin as with mastic-peptone compounds; the solubility relationships of a combination of this order depend on the proportions in which its components are mutually adsorbed; the greater the proportion of peptone present in such combinations the more easily is the peptone washed out of them by water; mastic-serum-albumin is insoluble in alcohol chloroform.

The Behaviour of Ferments.—An important résumé of already known lecithin-ferment combinations is given. A mastic-suspension mixed with a filtered solution of rennet was faintly acidified. The whole of the enzyme was contained in the resulting precipitate. By extracting this precipitate by various solvents and precipitating in various ways, a number of mastic-rennet combinations were obtained and the relationship was found to hold that the lower the mastic content the more readily was the rennet removed. It was further established experimentally that lecithin-rennet behaves in an analogous manner to mastic-rennet.

The precipitation reactions of mastic-trypsin, although analogous, differ considerably from those of mastic-rennet. G. S. W.

Action of Salts on the Fermenting Power of Different Diastatic Ferments. L. PRETI (*Biochem. Zeitsch.*, 1907, 4, 1—5).—Solutions of pancreatin, urine, and blood-serum, after dialysis, have no diastatic action on starch. Activity is restored by the addition of any one of a number of electrolytes. Takadiastase and maltin solutions cannot be rendered inactive by dialysis. G. S. W.

Chemistry of Silicon. ALBERT LADENBURG (*Ber.*, 1907, 40, 2274—2279).—*Triphenylbromosilicane*, $SiPh_3Br$, is formed when tetraphenylsilicane (Polis, Abstr., 1885, 973; 1886, 618) is heated with bromine, first at 100° and afterwards in tubes at 150°. It forms colourless, crystalline needles, m. p. 118—120°, fumes slightly in contact with the air, and is decomposed by water or alcohol.

Triphenylsilicol, obtained by heating the bromide with dilute potassium carbonate solution at 120°, separates from ether or acetone in small, transparent crystals, m. p. 148—150° (Polis, 139—140°). Its *acetyl* derivative melts at 96—97°. The silicol dissolves in fuming sulphuric acid yielding a *trisulphonic acid*, $OH\cdot Si(C_6H_4\cdot SO_3H)_3$, the *barium* salt of which crystallises from water in compact prisms. A *trinitro*-derivative of the barium salt, $C_{36}H_{20}O_{32}N_6S_6Ba_3Si$, has been obtained as a yellow, crystalline crust.

Diphenyldibromosilicane, $SiPh_2Br_2$, obtained by heating the monobromo-derivative with bromine at 150°, has b. p. 175—183°/12 mm., and with zinc ethyl yields *diphenyldiethylsilicane*, $SiEt_2Ph_2$, b. p. 305—320°.

Triphenylbromosilicane and zinc ethyl at 120° yield either *triphenylsilicane*, $SiHPh_3$, which crystallises from acetone in plates, m. p. 200—203°, or *triphenylethylsilicane*, $SiEtPh_3$, m. p. 72—74°.

J. J. S

Combination of Mixed Organo-magnesium Compounds with the Pyridine and Quinoline Bases. BERNARDO ODDO (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 413—418. Compare Abstr., 1904, i, 920; Sachs and Sachs, Abstr., 1904, i, 925).—In addition to the additive compounds of quinoline and magnesium phenyl bromide already obtained (*loc. cit.*), the author has prepared the *compound*, $(C_9H_7N)_3,MgPhBr$, in the form of an unstable yellow powder insoluble in all the neutral solvents.

Similar additive compounds containing four or more mols. of quinoline for 1 mol. of magnesium phenyl bromide are still more unstable than the above and could not be isolated.

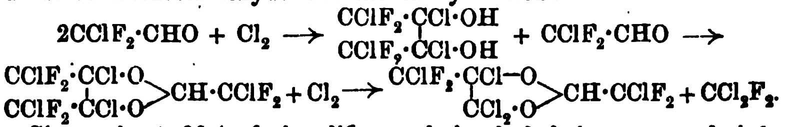
The simultaneous action of pyridine (1 mol.) and quinoline (1 mol.) on magnesium phenyl bromide also yields an unstable compound which is decomposed by water, giving pyridine and 2-phenylquinoline.

T. H. P.

Organic Chemistry.

Decomposition of Gaseous Hydrocarbons by Heating with Finely-divided Aluminium. M. I. Kusnetzoff (*Ber.*, 1907, 40, 2871—2873).—It is found that aluminium at temperatures near its melting point, like red-hot magnesium (Lidoff and Kusnetzoff, Abstr., 1906, ii, 201), decomposes methane, ethane, ethylene, and acetylene completely into their elements. The hydrogen and part of the carbon are obtained in the free state, whilst the remainder of the carbon combines with the aluminium, forming aluminium carbide. W. H. G.

Chlorination of Difluoroethyl Alcohol. Frédéric Swarts (*Bull. Acad. roy. Belg.*, 1907, 339—358).—Under the influence of sunlight, chlorine attacks difluoroethyl alcohol fairly rapidly at first, but more slowly afterwards, and the action is not complete after several weeks. The products of an experiment lasting twenty-six days consisted of (1) *difluorochloroacetyl chloride*, $CClF_2\cdot COCl$, a colourless, very mobile liquid having an irritating odour, b. p. 34°, and fuming strongly in air. It reacts violently with water and alcohol to form the corresponding acid (Abstr., 1906, i, 478) and ester. (2) Difluorochloroacetic acid, formed from the chloride by the action of water vapour, the presence of which cannot be avoided in an experiment of such long duration. (3) A *polymeride* of difluorochloroacetyl chloride, a liquid, b. p. 134°, which is slowly attacked by water and rapidly by alcohol, giving the (non-polymerised) acid and ester. It is partially depolymerised on distillation. Vapour density determinations give it a polymerisation coefficient of 1·82 at 100°/161—163·1 mm., 1·75 at 137·5°/176·6 mm., and 1·59 at 208°/149 mm., but the depolymerisation is not reversible by lowering the temperature. Cryoscopic determinations give a polymerisation coefficient slightly above 2, unaltered by dilution. The formula $COCl\cdot CCl{<}\begin{smallmatrix}F\cdot F\\ F\cdot F\end{smallmatrix}{>}CCl\cdot COCl$ is suggested for the polymeride. When treated in benzene solution with gaseous ammonia, it gives *difluorochloroacetamide*, $CClF_2\cdot CO\cdot NH_2$, in the form of tabular crystals, m. p. 78·5°, identical with the product from ethyl difluorochloroacetate. (4) *Carbon difluorodichloride*, CCl_2F_2, a gas, b. p. −25°. (5) A small quantity of a substance, b. p. 170°, smelling like chloralide. The author suggests the following scheme in explanation of the formation of the last two substances, supposing that difluorochloroacetaldehyde is momentarily formed :



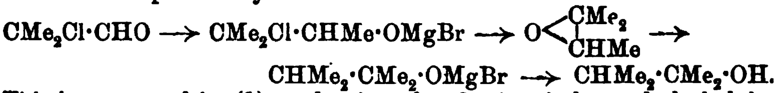
$$2CClF_2\cdot CHO + Cl_2 \longrightarrow \begin{array}{l} CClF_2\cdot CCl\cdot OH \\ CClF_2\cdot CCl\cdot OH \end{array} + CClF_2\cdot CHO \longrightarrow$$

$$\begin{array}{l} CClF_2\cdot CCl\cdot O \\ CClF_2\cdot CCl\cdot O \end{array}{>}CH\cdot CClF_2 + Cl_2 \longrightarrow \begin{array}{l} CClF_2\cdot CCl-O \\ CCl_2\cdot O \end{array}{>}CH\cdot CClF_2 + CCl_2F_2.$$

Since about 80% of the difluoroethyl alcohol is converted into difluorochloroacetyl chloride and the corresponding acid, the author considers that the principal reaction is that represented by the equation $CHF_2\cdot CH_2\cdot OH + 3Cl_2 = CClF_2\cdot COCl + 4HCl$.

In an incomplete chlorination, difluoroacetyl chloride and what is probably a polymeride of the latter are also formed. E. H.

Various Syntheses with Compounds Containing the Group $CMe_2Cl\cdot C\vdots$. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 162—189).—In the esters of carboxylic acids containing the radicles $\cdot CH_2Cl$ or $\cdot CHMe\cdot Cl$, only the carboxylic group is attacked by magnesium methyl bromide, whilst in esters containing the group $\cdot CMe_2Cl$, both the chlorine and the alkyloxy-group are replaced by methyl. Thus ethyl chloroacetate gives chloro*tert.*butyl alcohol, whilst ethyl chloro*iso*butyrate gives pentamethylethanol (Abstr., 1906, i, 782). But chloro*iso*butaldehyde in ethereal solution when added to an ethereal solution of magnesium methyl bromide, instead of giving the expected pinacolyl alcohol, gives the isomeric $\alpha\alpha\beta$-trimethylpropyl alcohol, $CHMe_2\cdot CMe_2\cdot OH$. The formation of the latter cannot be due to the intramolecular change of the pinacolyl alcohol first formed, since changes of this kind are only known with the corresponding halides, but is best explained by the scheme:



$$CMe_2Cl\cdot CHO \longrightarrow CMe_2Cl\cdot CHMe\cdot OMgBr \longrightarrow O\!<\!\begin{matrix}CMe_2\\ |\\ CHMe\end{matrix} \longrightarrow CHMe_2\cdot CMe_2\cdot OMgBr \longrightarrow CHMe_2\cdot CMe_2\cdot OH.$$

This is supported by (1) production of $\alpha\alpha\beta$-trimethylpropyl alcohol by the action of magnesium methyl bromide on trimethylethylene oxide; (2) the different course followed by the reaction when oxide-formation is impossible owing to the absence of the $CH\cdot O\cdot MgBr$ group; thus when an ethereal solution of magnesium methyl bromide (1 mol.) is added to an ethereal solution of $\alpha\beta$-dichloro-β-methylpropyl *iso*butyl ether, $CMe_2Cl\cdot CHCl\cdot OC_4H_9(iso)$, *$\beta$-chloro-$\alpha\beta$-dimethylpropyl* iso*butyl ether*, $CMe_2Cl\cdot CHMe\cdot OC_4H_9(iso)$, is formed as a strongly smelling, highly refractive, colourless liquid, b. p. 178—179°/774 mm., D^{20} 0·9048, n_D 1·42711, whilst by adding the solution of the ether to that of magnesium methyl bromide (2 mols.), *β-*iso*butyl-β-*iso*amyl ether*, $CMe_2:CMe\cdot OC_4H_9(iso)$, is produced, a colourless liquid, b. p. 160—161°, D^{20} 0·7952, n_D 1·41692, which has a powerful smell and combines readily with bromine (compare Vitoria, *Bull. Acad. roy. Belg.*, 1901, 1087).

When the ethereal solution of magnesium methyl bromide is added to that of chloro*iso*butaldehyde, besides $\alpha\alpha\beta$-trimethylpropyl alcohol, the chlorohydrin, $CHMeCl\cdot CMe_2\cdot OH$, and the bromohydrin,

$$CHMeBr\cdot CMe_2\cdot OH,$$

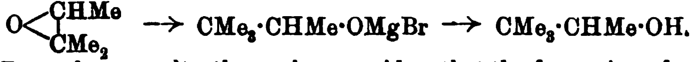
are formed, probably from the action of magnesium methyl bromide on trimethylethylene oxide (compare Grignard, Abstr., 1903, i, 552).

Rizza's preparation of $\alpha\alpha\beta$-trimethylpropyl alcohol by the action of excess of zinc-methyl on chloral (Abstr., 1882, 491) can be explained by a scheme similar to the above.

$\alpha\alpha\beta$-Trimethylpropyl alcohol is also formed by the action of magnesium methyl bromide on β-*iso*amylene chlorohydrin,

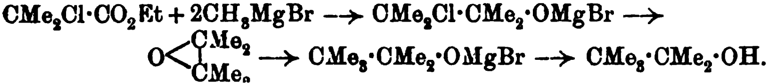
$$CMe_2Cl\cdot CHMe\cdot OH,$$

and whichever way it is prepared it always reacts with bromine, probably owing to the presence of a trace of Friedel's pinacolyl alcohol, formed by the alternative reaction of trimethylethylene oxide with magnesium methyl bromide,



$$O<\begin{matrix}CHMe\\ |\\ CMe_2\end{matrix} \rightarrow CMe_3\cdot CHMe\cdot OMgBr \rightarrow CMe_3\cdot CHMe\cdot OH.$$

From these results, the author considers that the formation of pentamethylethanol from ethyl chloro*iso*butyrate is explained by the scheme:



$$CMe_2Cl\cdot CO_2Et + 2CH_3MgBr \rightarrow CMe_2Cl\cdot CMe_2\cdot OMgBr \rightarrow$$
$$O<\begin{matrix}CMe_2\\ |\\ CMe_2\end{matrix} \rightarrow CMe_3\cdot CMe_2\cdot OMgBr \rightarrow CMe_3\cdot CMe_2\cdot OH.$$

Pentamethylethanol is also produced by the action of magnesium methyl bromide on Friedel's pinacolin, $CMe_3\cdot COMe$, on tetramethylethylene oxide, or on *β-chloro-ααβ-trimethylpropyl alcohol*, $CMe_2Cl\cdot CMe_2\cdot OH$, a liquid, b. p. 151—152°, which reacts with potash, giving tetramethylethylene oxide. E. H.

Velocity of Addition of Iodine to Allyl Alcohol. WALTER HERZ and BRUNO MYLIUS (*Ber.*, 1907, **40**, 2898—2904).—The reaction $C_3H_5\cdot OH + I_2 \rightleftharpoons C_3H_5I_2\cdot OH$ proceeds almost to completion (compare Bauer and Moser, this vol., i, 307). The constant K, calculated for a bimolecular reaction, varies largely with the nature of the solvent. In carbon tetrachloride or chloroform at 25° it is fairly steady and independent of the initial concentrations, provided that the concentration of the alcohol is much greater than that of the iodine. In carbon disulphide the value of K is dependent on the initial concentration of the alcohol (compare Burke and Donnan, Trans., 1904, **85**, 553). The constant has been determined in mixtures of these solvents, and the results are expressed graphically. If the concentration of the alcohol is regarded as a constant, the value of K, calculated for a unimolecular reaction, varies with the initial concentration of the alcohol, and the reaction is pseudo-unimolecular. C. S.

Action of Sodium Arsenite on Sodium Ethyl Thiosulphate. AUGUST GUTMANN (*Ber.*, 1907, **40**, 2818—2822).—The action of sodium arsenite on sodium ethyl thiosulphate in the presence of sodium hydroxide takes place in accordance with the equation:

$$2NaEtS_2O_3 + 2NaOH + 2Na_3AsO_3 = 2Na_2SO_3 + 2EtSH + 2Na_3AsO_4.$$

The amounts of sodium sulphite and arsenate and of mercaptan formed were estimated.

Sodium ethyl thiosulphate does not interact with $N/10$ iodine solution, it does not dissolve silver haloids, does not decolorise a blue solution of a cupric salt, and does not form potassium thiocyanate with potassium cyanide. A. McK.

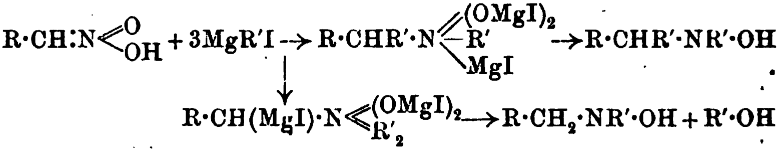
Action of Magnesium or Zinc Alkyl Iodides on Esters of Nitrous Acid and on Nitroparaffins. IWAN BEWAD (*Ber.*, 1907, **40**, 3065—3083).—In the preparation of β-dialkylhydroxylamines the zinc alkyl usually employed can be replaced advantageously by zinc alkyl iodides or magnesium alkyl iodides when esters of nitrous acid are used, but not in the case of nitroparaffins. The reactions have been examined between zinc *iso*propyl iodide and *iso*amyl nitrite, zinc *iso*propyl iodide and nitroethane, zinc ethyl iodide and *iso*amyl nitrite, zinc ethyl iodide and nitroethane, magnesium propyl iodide and *iso*propyl nitrite, magnesium propyl iodide and nitroethane, magnesium ethyl iodide and nitropropane, and magnesium ethyl iodide and nitroethane. Ethereal solutions of the reacting substances are mixed slowly at 0°; where zinc compounds are employed, the mixture is kept for three to seven weeks before being decomposed with cold water. The products have been described (Bewad, Abstr., 1900, i, 629; *J. pr. Chem.*, 1901, **63**, 94, 193; Mouren, Abstr., 1901, i, 317).

The reactions proceed as follows:

$$\text{(I.)}\ \mathrm{RO{\cdot}NO + 2ZnR'I \longrightarrow ZnI{\cdot}O{\cdot}NR'_2(OR){\cdot}ZnI \longrightarrow R{\cdot}OH + R'_2N{\cdot}OH.}$$

$$\text{(II.)}\ \mathrm{R{\cdot}CH_2{\cdot}NO_2 \longrightarrow R{\cdot}CH{:}NO{\cdot}OH + 2ZnR'I \longrightarrow R{\cdot}CHR'{\cdot}NR(OZnI)_2{\cdot}ZnI \longrightarrow R{\cdot}CHR'{\cdot}NR'{\cdot}OH.}$$

Magnesium alkyl iodides react with esters of nitrous acid in a similar manner to the zinc compounds; with nitroparaffins the reaction follows two courses:



$$\begin{tikzcd}
\mathrm{R{\cdot}CH{:}N{<}^{O}_{OH} + 3MgR'I} \arrow[r] \arrow[d] & \mathrm{R{\cdot}CHR'{\cdot}N{\lessgtr}\begin{smallmatrix}(OMgI)_2\\ R'\\ MgI\end{smallmatrix}} \arrow[r] & \mathrm{R{\cdot}CHR'{\cdot}NR'{\cdot}OH} \\
\mathrm{R{\cdot}CH(MgI){\cdot}N{\ll}^{(OMgI)_2}_{R'_2}} \arrow[rr] & & \mathrm{R{\cdot}CH_2{\cdot}NR'{\cdot}OH + R'{\cdot}OH}
\end{tikzcd}$$

C. S.

The Phosphorus of Lecithin Prepared from Certain Seeds.

ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1907, **52**, 54—61).—Previous estimations of phosphorus in vegetable lecithins have given varying figures. Thus, that from the seeds of *Vicia sativa* and *Lupinus luteus* contain 3·68%, a number which lies near to the values calculated for di-oleyl-lecithin (3·68) and distearyl-lecithin (3·84), and lower than that calculated for dipalmityl-lecithin (4·12). A lower percentage (about 2) was obtained for the lecithin prepared from cereals. In view of the fact that such preparations were not pure and probably were contaminated with carbohydrates, it was considered desirable to make further analyses. The present paper relates to the lecithin prepared from *Lupinus luteus*, *Vicia sativa*, and *Pinus Cembra*; the percentages of phosphorus in these were respectively 3·46—3·76, 3·51—3·62, and 3·60.

W. D. H.

Phosphorus Percentage of various Samples of Protagon.

A. C. LOCHHEAD and WILHELM CRAMER (*Bio-Chem. J.*, 1907, **2**, 350—356).—The agreement between the phosphorus percentage of various samples of protagon prepared by different methods is regarded as evidence in favour of the view that protagon is a well-defined chemical substance. The figures given vary from 0·96% to 1·34%.

W. D. H.

Stannous Formate and its Decomposition Products. MARTIN GOLDSCHMIDT (*Chem. Zeit.*, 1907, **31**, 608).—The solution obtained by dissolving freshly precipitated stannous hydroxide in 30—40% formic acid yields on evaporation in a vacuum white, monoclinic crystals of anhydrous stannous formate. The salt decomposes into stannous oxide and formic acid when its solution in water, acidified with formic acid, is boiled. The dry salt is completely decomposed at temperatures slightly above 100°, the products of decomposition being stannous oxide, carbon dioxide, formaldehyde (chiefly as paraformaldehyde), and methyl formate, $3(HCO_2)_2Sn \longrightarrow 3CO_2 + 3SnO + H{\cdot}CHO + H{\cdot}CO_2Me$.

W. H. G.

Glucinum Acetates. HERMANN STEINMETZ (*Zeitsch. anorg. Chem.*, 1907, **54**, 217—222).—Basic glucinum acetate, Be_4Ac_6O, first prepared by Urbain and Lacombe (Abstr., 1902, i, 132, 418), crystallises from organic solvents in well formed, octahedral crystals which, on sublimation, change to doubly-refracting prisms and leaflets; the latter modifications are unstable at the ordinary temperature. From a solution of the basic acetate in cold pyridine, a double compound of the formula $Be_4Ac_6O,3C_5H_5N$ was obtained; the pyridine is very loosely combined.

Normal glucinum acetate, $Be(C_2H_3O_2)_2$, not previously known, was obtained by heating a mixture of equal parts of the basic acetate and glacial acetic acid with five to six parts of acetic anhydride for two hours at 140° in a sealed tube. It occurs in doubly-refracting, microscopic leaflets, which are insoluble in water as well as in alcohol, ether, and other organic solvents; on continued boiling with water it goes into solution and simultaneously suffers partial hydrolysis. It melts with decomposition above 300°, the basic acetate subliming.

The author considers that these results support the formula for the basic acetate advanced by Glassman (this vol., i, 109).

G. S.

Modified Nickel Acetate, a New Type of Excitant of Oxidation for Quinols. ANDRÉ JOB (*Compt. rend.*, 1907, **144**, 1266—1267).—Examination of the acetates of manganese and cobalt according to the very sensitive method previously described (Abstr., 1903, ii, 214; 1906, ii, 531) shows that the rapidity of oxidation by these salts is greater at first, and diminishes much more quickly in the first two than in the succeeding minutes. When pure nickel acetate is heated for a long time at 100°, it loses acetic acid, but remains soluble in cold water. The activity of the product in oxidising quinol exceeds that of manganese acetate. The activity of both manganese acetate and heated nickel acetate is diminished either by decreasing the amount present or by adding acetic acid. But whilst the first method renders the activity of manganese acetate less persistent and the second method renders it more stable, with nickel acetate both methods effect a rapid diminution in the rate of oxidation. Thus heated nickel acetate forms a new type of oxydase for quinol, its activity apparently depending on the presence of the hydroxide. Accordingly by comparing the activity of normal nickel acetate with that of modified nickel acetate, a method of estimating the degree of hydrolysis of the latter salt is obtained. The author finds for a *N*/100 solution, less than 1% is hydrolysed.

E. H.

Acetic Esters. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 285—313).—By the action of acetyl chloride or acetic anhydride on the magnesium halide compounds of the tertiary alcohols (compare Houben, Abstr., 1906, i, 520), or, in some cases, by the action of magnesium alkylhalides on the aldehydes, ketones, or esters from which the tertiary alcohols are prepared by Grignard's reaction, the following acetates have been obtained. $\alpha\alpha\beta$-Trimethylpropyl acetate, $CHMe_2{\cdot}CMe_2{\cdot}OAc$, a liquid, having D^{20} 0·9226, n_D 1·41831 (compare Kondakoff, Abstr., 1894, i, 113; Friedel, Abstr., 1873, 488), which is hydrolysed by distillation with solid potash, and is rapidly transformed by cold fuming hydrochloric acid into the *chloride*, a very mobile liquid, b. p. 111—113°. *αα-Dimethylbutyl acetate*, $CH_2Me{\cdot}CH_2{\cdot}CMe_2{\cdot}OAc$, a liquid, b. p. 142—143°/752 mm., D^{20} 0·9114, n_D 1·41433. *tert.*-Butyl acetate, $CMe_3{\cdot}OAc$, a liquid, b. p. 95°/750 mm. (Butleroff, *Annalen*, 1867, **144**, 7, gives 96°; Kondakoff gives 51°), D^{20} 0·8958, n_D 1·39469. Both of these esters react like the first towards alkalis and halogen acids. *ααββ-Tetramethylpropyl acetate*, $CMe_3{\cdot}CMe_2{\cdot}OAc$, a liquid with a faint camphor-like smell, b. p. 158—160°/766 mm., 96—97°/80 mm., D^{20} 0·8906, n_D 1·42611, m. p. −51°, which, when impure, is decomposed by distillation at the ordinary pressure, forming Butleroff's $\beta\gamma\gamma$-trimethyl-α-butylene (Abstr., 1875, 1248),

$$CMe_3{\cdot}CMe{:}CH_2,$$

a liquid having b. p. 78—80°/750 mm., D^{20} 0·7188. The acetate reacts very readily with the halogen acids, fuming hydrochloric acid, giving the *chloride* in the form of a white solid, m. p. 130°. On the other hand, it is not hydrolysed by an hour's boiling with alcoholic potash. Whilst primary and secondary alcohols readily form acetates when treated with acetyl chloride, and these acetates are attacked with difficulty by hydrochloric acid, the converse is true for the tertiary alcohols. The author shows that the difference between the boiling points of the acetates and those of the corresponding alcohols increases in passing from primary to tertiary, and that the acetylation of primary, secondary, and tertiary alcohols produces an increasing rise in the boiling point, as the radicle combined with the $\cdot CH_2{\cdot}OH$, $:CH{\cdot}OH$, and $\vdots C{\cdot}OH$ groups is increasingly methylated. E. H.

Theory of Saponification. II. JULIUS MARCUSSON (*Ber.*, 1907, **40**, 2905—2915. Compare Abstr., 1906, i, 924).—A reply to Lewkowitsch (this vol., i, 10). The high acetyl value of an incompletely hydrolysed fat is not due to the presence of mono- and diglycerides, but depends partly on the existence of acids soluble in water and of hydroxy-acids, and partly on the absorption of atmospheric oxygen. C. S.

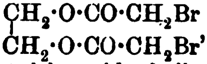
Peat Wax. ROMAN ZALOZIECKI and JOACHIM HAUSMANN (*Zeitsch. angew. Chem.*, 1907, **20**, 1141—1143).—A brownish-yellow wax is obtained from peat to the extent of about 1% by extraction with alcohol. This substance on treatment with ether is separated into two portions; the fraction readily soluble in ether forms a dark green, wax-like mass with an agreeable odour, whilst the insoluble fraction is a brown substance.

The soluble fraction yields on hydrolysis a greenish-coloured *acid*, m. p. 184°, which, from the results of analysis and molecular weight determinations, probably has the formula $C_{16}H_{25}O_5$, and an *alcohol*. This alcohol is identical in composition with that obtained from the portion insoluble in ether on hydrolysis; it is a yellow, gelatinous substance, m. p. 124—130°, and probably has the formula $C_{20}H_{40}O_4$. The *acid* which the insoluble portion yields on hydrolysis does not melt under 260°, and probably has the formula $C_{21}H_{35}O_7$.

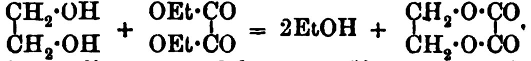
The authors consider that the wax obtained from peat is formed during the decomposition of the vegetable matter, and is not present as such in the original plants; they further maintain that peat wax is not identical with the wax obtained from algæ, as stated by Krämer and Spilker (Abstr., 1900, i, 73; 1902, i, 333), and is in no way connected with the formation of mineral oil. W. H. G.

Cyclic Esters from Ethylene Glycol and from Glycerol.

Carl A. Bischoff (*Ber.*, 1907, 40, 2803—2813).—Ethylene glycollate may be prepared either from glycollic acid and ethylene glycol or from monosodium ethylene glycol and ethyl chloroacetate in alcoholic solution or in suspension in benzene.

Ethylene bromoacetate,  $\begin{array}{l}CH_2\cdot O\cdot CO\cdot CH_2Br\\ | \\ CH_2\cdot O\cdot CO\cdot CH_2Br\end{array}$, obtained from monosodium glycol and bromoacetyl bromide, boils at 125—130°/20 mm.

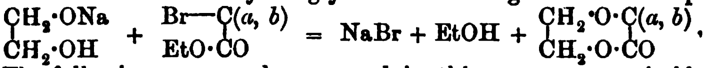
When glycol is heated with an excess of diethyl oxalate, the following reaction takes place:



$$\begin{array}{l}CH_2\cdot OH\\ | \\ CH_2\cdot OH\end{array} + \begin{array}{l}OEt\cdot CO\\ \quad\ \ | \\ OEt\cdot CO\end{array} = 2EtOH + \begin{array}{l}CH_2\cdot O\cdot CO\\ | \qquad\quad\ | \\ CH_2\cdot O\cdot CO\end{array}.$$

The resulting cyclic compound has m. p. 171—172°, and is isomeric with the compound with m. p. 143° (Bischoff and Walden, Abstr., 1895, i, 17).

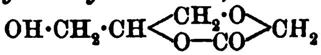
With monosodium ethylene glycol the following reaction takes place:



$$\begin{array}{l}CH_2\cdot ONa\\ | \\ CH_2\cdot OH\end{array} + \begin{array}{l}Br—C(a,\,b)\\ \quad\ \ | \\ EtO\cdot CO\end{array} = NaBr + EtOH + \begin{array}{l}CH_2\cdot O\cdot C(a,\,b)\\ | \qquad\quad\ | \\ CH_2\cdot O\cdot CO\end{array}.$$

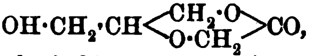
The following compounds, prepared in this manner, are viscid oils; *ethylene a-oxypropionate*, $C_5H_8O_3$, b. p. 119—120°/30 mm.; *ethylene a-oxybutyrate*, $C_6H_{10}O_3$, b. p. 104—106°/20 mm.; *ethylene a-oxyisobutyrate*, $C_6H_{10}O_3$, b. p. 105°/20 mm.; *ethylene a-oxyisovalerate*, $C_7H_{12}O_3$, b. p. 120—125°/17 mm.

Glyceroloxyacetolactone,



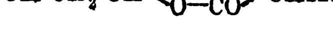
$$OH\cdot CH_2\cdot CH{<}\begin{array}{c}CH_2\cdot O\\ O—CO\end{array}{>}CH_2$$

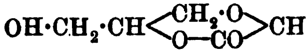
or



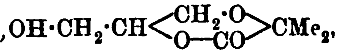
$$OH\cdot CH_2\cdot CH{<}\begin{array}{c}CH_2\cdot O\\ O\cdot CH_2\end{array}{>}CO,$$

obtained from monosodium glycerol and ethyl bromoacetate, is a viscid, yellow oil, b. p. 170—175°/5 mm.

Glycerol a-oxypropiolactone,  $OH\cdot CH_2\cdot CH{<}\begin{array}{c}CH_2\cdot O\\ O—CO\end{array}{>}CHMe$ (?), obtained from monosodium glycerol and ethyl α-bromopropionate, has b. p. 200—210°/13 mm.



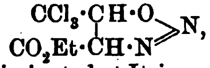
Glycerol α-oxybutyrolactone, $OH\cdot CH_2\cdot CH\left<\begin{matrix}CH_2\cdot O\\ O—CO\end{matrix}\right>CHEt$ (?), has b. p. 200—215°/10 mm.



Glycerol α-oxyisobutyrolactone, $OH\cdot CH_2\cdot CH\left<\begin{matrix}CH_2\cdot O\\ O—CO\end{matrix}\right>CMe_2$, has b. p. 185—195°/8 mm. A. McK.

Synthesis of β-Ketonic Esters by Means of Ethyl Diazoacetate.

FRITZ SCHLOTTERBECK (*Ber.*, 1907, 40, 3000—3002).—Ethyl γ-trichloroacetoacetate, $CCl_3\cdot CO\cdot CH_2\cdot CO_2Et$, is formed by the action of ethyl diazoacetate on chloral, the action probably being accompanied by the intermediate formation of the compound



$$\begin{matrix}CCl_3\cdot CH\cdot O\\ |\\ CO_2Et\cdot CH\cdot N\end{matrix}>N,$$

from which nitrogen is eliminated. It is a colourless liquid, D^{18} 1·41, b. p. 233—234° (corr.)/749 mm. and b. p. 118° (corr.)/11 mm. Mewes gives b. p. 223—225° and Genvresse b. p. 221—223°. Its alcoholic solution gives an intensely red coloration with ferric chloride.

A. McK.

New Synthesis of Suberic Acid by Means of Organomagnesium Compounds.

NICOLAI D. ZELINSKY and JOHANNES GUTT (*Ber.*, 1907, 40, 3049—3050).—In attempting to synthesise glutaric acid from trimethylene bromide, magnesium and carbon dioxide a small quantity of suberic acid was isolated, but no glutaric acid. There was also obtained trimethylene and propylene and neutral substances having no constant b. p. Suberic acid must be formed through the coalescing of two trimethylene residues to form hexamethylene-αζ-dimagnesium bromide. W. R.

Derivatives of Saccharin.

HEINRICH KILIANI, P. LOEFFLER, and O. MATTHES (*Ber.*, 1907, 40, 2999).—Parasaccharone (Abstr., 1904, i, 975), $[\alpha]_D$ −107·8°; the *barium* and *magnesium* salts are described.

The quinine salts have been used for the separation and identification of the saccharins (Abstr., 1904, i, 975); the rotatory power of these salts was determined as a possible means of identification, but the differences in the molecular rotations is found to be comparatively small. Quinine saccharate, $[\alpha]_D$ −102·6°; quinine *iso*saccharate, $[\alpha]_D$ −118·2°; quinine metasaccharate, $[\alpha]_D$ −89·5°, is soluble to the extent of 1 part in 25 parts of 50% alcohol; quinine parasaccharate, $[\alpha]_D$ −105·7°. G. Y.

Comparative Action of Barley Extracts and Malt on the More Resistant Dextrins.

JULES WOLFF (*Compt. rend.*, 1907, 144, 1368—1370. Compare this vol., i, 482).—Barley extract acted only feebly, and after forty-eight hours ceased to act altogether, whilst malt extract gradually transformed the dextrins into maltose.

N. H. J. M.

Oxalic Aldehyde [Glyoxal]. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 94—118).—The author has put forward the proposition that the accumulation of acid groups, $:CCl$, $:CO$, $\cdot CHO$, $\cdot CN$, &c., in neighbouring positions in carbon compounds increases their volatility, or that in a compound containing one of these groups the substitution of a second acid group in a position near the first causes a considerably less increase in boiling point than did the substitution of the first. Harries and Temme's unimolecular glyoxal (this vol., i, 183) is claimed as a fresh confirmation of this view, since its boiling point (51°) is only 30° above that of acetaldehyde, whereas the boiling point of the latter exceeds that of ethane by 111°. By the comparison of the boiling points of a large number of aldehydes, ketones, and alkyloxy-, keto-, and halogen-nitriles, it is shown that the rule no longer holds when the acid groups are separated by the group $\cdot CH_2\cdot CH_2\cdot$.

Other examples show that this influence of acid groups is the greater, the less the amount of hydrogen contained in the group displaced.

Unimolecular glyoxal is also an example of the rule that compounds containing the group $\cdot CO\cdot CO\cdot$ are coloured, and that the colour disappears when the $CO:$ groups are reduced to $:CH\cdot OH$ or $:CH_2$ groups. E. H.

Preparation of Some Aliphatic Ethers of ortho-Ketones. Preparation of Esters of ortho-Acids. H. REITTER and EDGAR HESS (*Ber.*, 1907, 40, 3020—3025).—Homologues of Claisen's acetone orthoethyl ether, $CMe_2(OEt)_2$, are described. One of the methods given by Claisen for the preparation of the latter substance was by means of nascent orthoformic ester, that is, from formiminoether and alcohol, thus: $COMe_2 + OEt\cdot CH:NH_2Cl + 2EtOH = NH_4Cl + H\cdot CO_2Et + CMe_2(OEt)_2$. The authors find that higher homologues are obtained by replacing the anhydrous hydrogen cyanide necessary in Claisen's reaction by acetonitrile, propionitrile, and phenylacetonitrile respectively.

Contrary to the experience of Pinner, the nitriles of acetic and propionic acids may be converted into esters of ortho-acids. The reaction, $OEt\cdot CR:NH_2Cl + 2EtOH = NH_4Cl + CR(OEt)_3$, proceeds without the addition of a ketone.

Orthomethylethylketone diethyl ether, $CMeEt(OEt)_2$, obtained from methyl ethyl ketone, absolute alcohol, and acetoiminoether hydrochloride, has b. p. 120°.

Orthodiethylketone diethyl ether, $CEt_2(OEt)_2$, obtained from diethyl ketone, alcohol, and acetoiminoether hydrochloride, has b. p. 154°.

Orthodipropylketone diethyl ether, $CPr_2(OEt)_2$, has b. p. 69—70°/12 mm.

Ethyl orthoacetate, $CMe(OEt)_3$, has b. p. 145—146°/748 mm.

Ethyl orthopropionate, $CEt(OEt)_3$, has b. p. 161°/766 mm.

A. McK.

Colloidal Properties of Starch. EUGÈNE FOUARD (*Compt. rend.*, 1907, 144, 1366—1368. Compare this vol., i, 391).—The stronger mineral acids, including sulphurous, phosphorous, and hydrofluosilicic acids, coagulate soluble starch, but the weak acids, including organic acids, carbonic and boric acids, and complex inorganic acids, such as silico- and phospho-tungstic acids, exert no coagulative action. There is a limit of concentration for each coagulating acid, beyond which it exerts no action, and this limit is the lower the more completely the acid is ionised. Hardy and Perrin's rule that at equal concentrations in hydrogen ions the acids have the same coagulating power, applies therefore, with the reservation, that an excess of ions or neutral molecules exerts an antagonistic action to coagulation.

The addition of alkalis to soluble starch retards coagulation, and the efficiency of the four alkalis tried are in the descending order, potassium hydroxide, lime, baryta, ammonia, and the rule holds that all alkaline solutions at equal concentration of hydroxyl ions exert the same retarding action. Excess of alkali inhibits coagulation altogether. Baryta behaves in an anomalous manner, owing to its reacting with the soluble starch, and it is for this reason that it falls below lime as a retarding agent.

Carefully purified starch can be converted into the soluble variety by prolonged contact with water at 60°. T. A. H.

Action of Nitric Acid on Starch. A. G. Doroschewsky and Adam Rakowsky (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 427—439).—The inversion of potato starch by means of nitric acid proceeds in several stages, the last one of which is of a unimolecular character. When the experiments are conducted in sealed tubes, the time taken for complete inversion is inversely proportional to the strength of acid employed (Abstr., 1884, **46**, 36), but acids above 0·4% result in the oxidation of the sugar to the corresponding acid. Whilst other investigators, using hydrochloric and sulphuric acids (*Zeit. anal. Chem.*, 1896, **35**, 609), have shown that the factor for calculating dextrose into starch is 0·917—0·941, for nitric acid it is 0·907, the theoretical being 0·900. To determine what sugars are actually produced after the disappearance of a certain amount of dextrin, their osazones have been prepared, but they have not been identified finally so far. Z. K.

Preparation of Quaternary Ammonium Bases by Means of Alkali from Additive Products of Tertiary Amines with Alkylene Dibromides. R. Lucius (*Arch. Pharm.*, 1907, **245**, 246—258).—Ethylene and trimethylene dibromides, when heated with trimethylamine, triethylamine, tribenzylamine, or tropine, unite with 1 or 2 mols. of the base. When the additive products are heated with alcoholic potassium hydroxide, potassium bromide is precipitated and a solution of the quaternary base is obtained; in the case of the additive products with 1 mol. of the base, the alkyl halogen atom is eliminated at the same time along with an atom of hydrogen, an unsaturated derivative being formed. For instance, trimethylene dibromide and trimethylamine form the compounds

$$CH_2(CH_2{\cdot}NMe_3Br)_2$$

and $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br$ (the first is the less soluble of the two);

these yield solutions of the bases $CH_2(CH_2{\cdot}NMe_3{\cdot}OH)_2$ and $CH_2{:}CH{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$ respectively. Most of the bases were isolated and analysed in the form of platinichlorides. The formulæ and melting points of the new substances described are enumerated below (the platinichlorides decomposed as they melted).

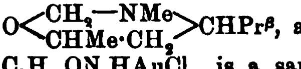
From ethylene dibromide. With triethylamine: $C_2H_4(NEt_3Br)_2$, 245—246°; $C_2H_4[NEt_3]_2PtCl_6$, 211°; $CH_2Br{\cdot}CH_2{\cdot}NEt_3Br$, 241—242°; $[CH_2Br{\cdot}CH_2{\cdot}NEt_3]_2PtCl_6$, 237—238°; $[CH_2{:}CH{\cdot}NEt_3]PtCl_6$, 208°. With tribenzylamine: $CH_2Br{\cdot}CH_2{\cdot}N(CH_2Ph)_3Br$, 263°; $[CH_2Br{\cdot}CH_2{\cdot}N(CH_2Ph)_3]_2PtCl_6$, 226—227°; $[CH_2{:}CH{\cdot}N(CH_2Ph)_3]PtCl_6$, 216°.

From trimethylene dibromide. With trimethylamine: $CH_2[CH_2{\cdot}NMe_3]_2PtCl_6$, 274—275°; $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Br$, 208°; $[CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3]PtCl_6$, 258—259°. With triethylamine: $CH_2(CH_2{\cdot}NEt_3Br)_2$, 245°; $CH_2[CH_2{\cdot}NEt_3]_2PtCl_6$, 220°; $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_3Br$, 227—228°; $[CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_3]_2PtCl_6$, 247—249°; $[CH_2{:}CH{\cdot}CH_2{\cdot}NEt_3]_2PtCl_6$, 213°. With tribenzylamine: $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_2Ph)_3Br$, 259—260; $[CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_2Ph)_3]_2PtCl_6$, 230—231°; $[CH_2{:}CH{\cdot}CH_2{\cdot}N(CH_2Ph)_3]_2PtCl_6$, 218—219°. With tropine: $CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}N(C_8H_{15}O)Br$, 310°; $[CH_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}N(C_8H_{15}O)]_2PtCl_6$, 255°; $[CH_2{:}CH{\cdot}CH_2{\cdot}N(C_8H_{15}O)]_2PtCl_6$, 253—254°.

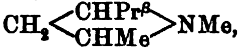
C. F. B.

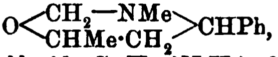
Preparation of Amino-alcohols from Unsaturated Methyl Ketones. I. MORITZ KOHN (*Monatsh.*, 1907, 28, 423—437).—An investigation to see whether methyl ketones, similar in constitution to mesityl oxide, combine like this compound with amines (Hochstetter and Kohn, Abstr., 1904, i, 18; Kohn, 1904, i, 932). It is found that *iso*butylidenacetone and benzylidenacetone combine with methylamine, forming ketonic bases, which when reduced with sodium amalgam yield the corresponding amino-alcohols.

Methyl-β-methylaminoisoamylcarbinol (*γ-methylamino-β-methylhexane-ε-ol*), $CHMe_2{\cdot}CH(NHMe){\cdot}CH_2{\cdot}CHMe{\cdot}OH$, prepared by reducing with sodium amalgam a hydrochloric acid solution of the ketonic amine which results by combining *iso*butylidenacetone with methylamine, is a colourless oil, b. p. 199—202°. When treated with methyl iodide, the tertiary base yields an oily *methiodide*, which when treated successively with silver and auric chlorides yields the *aurichloride*, $C_{10}H_{23}ON,HAuCl_4$, in the form of scaly crystals, m. p. 105—114°.

With formaldehyde, the amino-alcohol forms 3 : 6-*dimethyl*-4-iso-*propyltetrahydro*-1 : 3-*oxazine*,  $O{<}\begin{matrix}CH_2-NMe\\CHMe{\cdot}CH_2\end{matrix}{>}CHPr^{\beta}$, an oil, b. p. 179—181°; the *aurichloride*, $C_9H_{19}ON,HAuCl_4$, is a sandy powder; the *platinichloride*, $(C_9H_{19}ON)_2,H_2PtCl_6$, is a yellowish-red, crystalline substance. The *methiodide*, when treated successively with silver and auric chlorides, yields the *aurichloride*, $C_{10}H_{21}ON,HAuCl_4$, which crystallises in short needles, m. p. 136—139°. When treated with hydrogen bromide, methyl-β-methylamino*iso*amylcarbinol is converted into *ε-bromo-γ-methylamino-β-methylhexane hydrobromide*,

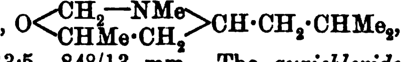
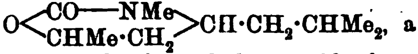
$$CHMeBr\cdot CH_2\cdot CH(NHMe)\cdot CHMe_2,HBr,$$

which on treatment with 33% aqueous potassium hydroxide is converted into 1 : 2-*dimethyl*-4-iso*propyltrimethylenimine*,  $CH_2<\begin{matrix}CHPr^\beta\\CHMe\end{matrix}>NMe$, a colourless, limpid liquid, b. p. 125—129°; the *aurichloride* is an oil; the *picrate*, $C_{14}H_{20}O_7N_4$, crystallises in glistening needles, m. p. 128—131°. The *methiodide* on successive treatment with silver and auric chlorides forms the *aurichloride*, obtained as a precipitate; the *platinichloride*, $(C_9H_{19}N)_2,H_2PtCl_6$, forms small, brilliant, granular crystals. In the same manner are obtained the *ethiodide*, the *aurichloride*, $C_{10}H_{21}N,HAuCl_4$, which forms small, woolly needles, and the *platinichloride*, $(C_{10}H_{21}N)_2,H_2PtCl_6$, a yellowish-red precipitate.

a-Methylamino-a-phenylbutane-γ-ol, $NHMe\cdot CHPh\cdot CH_2\cdot CHMe\cdot OH$, is prepared by the reduction of the compound obtained by the interaction of methylamine with benzylideneacetone. It crystallises from light petroleum in white, fibrous needles, m. p. 56—57°; b. p. 153—154°/17—18 mm.; the *picrate*, $C_{17}H_{20}O_8N_4$, forms granular crystals, m. p. 140°. From the *methiodide* of the *methyl ether* an *aurichloride*, $C_{18}H_{21}ON,HAuCl_4$, was prepared, which crystallises in light yellow leaflets, m. p. 131—134°. The *nitroso*-derivative, $C_{11}H_{16}O_2N_2$, is obtained by acting on the amino-alcohol with nitrous acid as a thick, yellow oil. Formaldehyde unites with the amino-alcohol with the formation of 4-*phenyl*-3 : 6-*dimethyltetrahydro*-1 : 3-*oxazine*,  $O<\begin{matrix}CH_2—NMe\\CHMe\cdot CH_2\end{matrix}>CHPh$, a colourless oil, b. p. 134°/15 mm.; the *aurichloride*, $C_{12}H_{17}ON,HAuCl_4$, melts at 153—157°.

W. H. G.

Preparation of Amino-alcohols from Unsaturated Methyl Ketones. II.

Moritz Kohn and Jakov Giaconi (*Monatsh.*, 1907, 28, 461—478. Compare preceding abstract).—The compound, obtained by the addition of methylamine to *a-iso*methylheptenone, yields when reduced in hydrochloric acid solution with sodium amalgam *methyl-β-methylaminoisoheptylcarbinol* (*δ-methylamino-β-methylheptane-ζ-ol*), $CHMe_2\cdot CH_2\cdot CH(NHMe)\cdot CH_2\cdot CHMe\cdot OH$, a colourless liquid, b. p. 106—107°/16 mm.; the *aurichloride* and *platinichloride* are resinous. The *methiodide* yields, on successive treatment with silver and auric chlorides, the *aurichloride*, $C_{11}H_{25}ON,HAuCl_4$, which crystallises in shining, yellow scales, m. p. 120°. The *nitroso*-derivative, $C_9H_{20}O_2N_2$, is a dark yellow oil. The amino-alcohol condenses with formaldehyde, forming 3 : 6-*dimethyl*-4-iso*butyltetrahydro*-1 : 3-*oxazine*,  $O<\begin{matrix}CH_2—NMe\\CHMe\cdot CH_2\end{matrix}>CH\cdot CH_2\cdot CHMe_2$, a colourless, mobile liquid, b. p. 83·5—84°/13 mm. The *aurichloride*, $C_{10}H_{21}ON,HAuCl_4$, is a light yellow powder, m. p. 134° (decomp.); the *platinichloride*, $(C_{10}H_{21}ON)_2,H_2PtCl_6$, forms orange-red needles; the *picrate* is an oil. On successive treatment with methyl iodide, silver and auric chlorides, the base forms the *aurichloride*, $C_{11}H_{23}ON,HAuCl_4$, a crystalline substance, m. p. 123—124° (decomp.); the *platinichloride*, $(C_{11}H_{23}ON)_2,H_2PtCl_6$, is a red substance, m. p. 134—135°. The amino-alcohol condenses with ethyl chlorocarbonate, forming 2-*oxy*-3 : 6-*dimethyl*-4-iso*butyltetrahydro*-1 : 3-*oxazine*,  $O<\begin{matrix}CO—NMe\\CHMe\cdot CH_2\end{matrix}>CH\cdot CH_2\cdot CHMe_2$, a pale yellow oil, b. p. 170·5°/11 mm., and with ethylene oxide, forming the *basic glycol*, $OH\cdot CHMe\cdot CH_2\cdot CH(CH_2Pr^{\beta})\cdot NMe\cdot CH_2\cdot CH_2\cdot OH$, a thick, colourless liquid, b. p. 161—162°/13 mm.; the *aurichloride*, obtained at first as a light yellow precipitate, quickly changes into an oil. The *compound*, obtained by heating the amino-alcohol with concentrated hydrobromic acid in a sealed tube at 95—100°, is converted by 50% potassium hydroxide into 1 : 2 *dimethyl*-4-iso*butyltrimethylenimine*, $CH_2<\begin{matrix}CH(C_4H_9)\\CHMe\end{matrix}>NMe$, a colourless, mobile liquid, b. p. 152—154°; the *aurichloride* is an unstable oil; the *picrate* crystallises in light yellow needles, m. p. 93—94°. The *methiodide* can be converted into the corresponding *aurichloride*, $C_{10}H_{21}N,HAuCl_4$, a pale yellow, crystalline substance, m. p. 63—64°; the *platinichloride*, $(C_{10}H_{21}N)_2,H_2PtCl_6$, forms small, pale red crystals decomposing at 170—171°. The *ammonium* base, formed by the action of moist silver oxide on the methiodide, loses water when distilled with 50% potassium hydroxide, yielding an *unsaturated* base, $C_{10}H_{21}N$, which is obtained as a colourless, mobile liquid, b. p. 168—171°; the *aurichloride* is an oil; the *platinichloride*, $(C_{10}H_{21}N)_2,H_2PtCl_6$, is a crystalline substance, m. p. 135—138°; the *picrate* crystallises in long, pale yellow needles, m. p. 84—85°. The *additive* compound, formed with methyl iodide, yields on successive treatment with silver and auric chlorides the *aurichloride*, $C_{11}H_{23}N,HAuCl_4$, obtained as a light yellow precipitate, m. p. 75—80°; the *platinichloride*, $(C_{11}H_{23}N)_2,H_2PtCl_6$, forms small, pale red crystals, m. p. 155—156°. When treated with moist silver oxide, the methiodide yields an *ammonium* base, which on distillation with water decomposes into trimethylamine, water, and an unsaturated *hydrocarbon*, C_8H_{14}; this is a colourless, mobile liquid, b. p. 120—122°, with a decided turpentine-like odour. One mol. of the hydrocarbon in carbon tetrachloride solution combines with 1 mol. of bromine at the ordinary temperature.

W. H. G.

Derivatives of Diacetonalkamine. VI. Moritz Kohn and Otto Morgenstern (*Monatsh.*, 1907, 28, 479—508. Compare Kohn, Abstr., 1904, i, 378, 932, 933; 1905, 928; this vol., i, 338).—Various diacetonalkamines have been prepared and their derivatives investigated.

Ethyldiacetonalkamine combines with hydrogen bromide, forming δ-*bromo*-β-*ethylamino*-β-*methylpentane hydrobromide*, $\cdot CHMeBr\cdot CH_2\cdot CMe_2\cdot NHEt,HBr$, since this compound when treated with concentrated potassium hydroxide is converted into 2 : 4 : 4-*trimethyl*-1-*ethyltrimethylenimine*, $CH_2<\begin{matrix}CMe_2\\CHMe\end{matrix}>NEt$, a colourless, mobile liquid, b. p. 117—118°. The *aurichloride*, $C_8H_{17}N,HAuCl_4$, is a powder, m. p. 115—116°; the *platinichloride*, $(C_8H_{17}N)_2,H_2PtCl_6$, crystallises in hexagonal prisms and decomposes at 170°; the *picrate*, $C_{14}H_{20}O_7N_4$, forms yellow needles, m. p. 176·5—177·5° (decomp.). The *methiodide* is identical with the ethiodide of 1:2:4:4-tetramethyltrimethylenimine (see this vol., i, 339). When treated with moist silver oxide, the methiodide is converted into an *ammonium* base, which when distilled with strong potassium hydroxide loses water and yields an unsaturated *base*, $C_9H_{19}N$, a colourless liquid, b. p. 154—156°, with a disagreeable odour; the *aurichloride* is an unstable oil; the *platinichloride*, $(C_9H_{19}N)_2,H_2PtCl_6$, forms prismatic crystals, m. p. 159—160°; the *picrate* is a crystalline substance, m. p. 85·5—86·5°; the *picrolonate* is a yellow powder, m. p. 137°. The base combines with methyl iodide, forming a *methiodide*, which on successive treatment with silver and auric chlorides is converted into the *aurichloride*, $C_{10}H_{21}N,HAuCl_4$, a coarse powder; the *platinichloride*, $(C_{10}H_{21}N)_2,H_2PtCl_6$, crystallises in prisms, m. p. 155—156° (decomp.). The methiodide on treatment with moist silver oxide is converted into an *ammonium* base, which on distillation with water decomposes, forming dimethylethylamine (Knorr and Pschorr, Abstr., 1905, i, 922), water, and a *hydrocarbon*, C_6H_{10}, b. p. 74—75°. This hydrocarbon is oxidised by potassium permanganate with the formation of acetone, acetic acid, and formic acid, and by nitric acid with the formation of oxalic acid. From its mode of formation and behaviour on oxidation, the hydrocarbon probably has the formula $CMe_2\colon CH\cdot CH\colon CH_2$, and the base from which it is derived is therefore probably *δ-methylethylamino-δ-methyl-*Δ^{α}*-amylene*,

$$NMeEt\cdot CMe_2\cdot CH\cdot CH\colon CH_2.$$

Methylethyldiacetonalkamine [*methyl-β-methylethylaminoisobutylcarbinol*], $OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NMeEt$, is prepared by the interaction of methyldiacetonalkamine and ethyl iodide. It is a colourless liquid, b. p. 197—198°; the *benzoate*, $C_{16}H_{25}O_2N$, is a colourless, viscid liquid, b. p. 177°/15 mm.; the *platinichloride*, $2C_9H_{21}ON,H_2PtCl_6$, crystallises in the regular system; the *aurichloride* is an unstable powder; the *picrate* is an oil. From the *methiodide* are formed the corresponding *aurichloride*, $C_{10}H_{23}ON,HAuCl_4$, obtained as a fine powder, m. p. 90°, and the crystalline *platinichloride*, $(C_{10}H_{23}ON)_2,H_2PtCl_6$.

Methylethyldiacetonalkamine combines with hydrogen bromide, forming a compound which is converted by potassium hydroxide into an unsaturated *base*, $C_9H_{19}N$, b. p. 154—156°, identical with that obtained from the methiodide of 2:4:4-trimethyl-1-ethyltrimethylenimine. W. H. G.

Derivatives of Diacetonalkamine. VII. MORITZ KOHN and KARL SCHLEGL (*Monatsh.*, 1907, **28**, 509—528).—Ethanoldiacetonalkamine (Kohn, Abstr., 1905, i, 928) has been further investigated and the formula previously given to this compound shown to be correct. Several derivatives of methyldiacetonalkamine are also described.

Ethanoldiacetonalkamine, when heated with acetic anhydride, is converted into the *diacetate*, $C_9H_{19}N(OAc)_2$, a colourless liquid, b. p. 160°/17 mm. When oxidised by chromic acid, ethanoldiacetonalkamine is converted into sarcosine (methylglycine), acetone, acetic acid, and carbon dioxide.

Methylallyldiacetonalkamine [*methyl-β-methylallylaminoisobutylcarbinol*], $OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NMe\cdot C_3H_5$, is obtained by the action of allyl iodide on methyldiacetonalkamine as a colourless oil, b. p. 212—215°; the *aurichloride* is an oil; the *platinichloride*,

$$(C_{10}H_{21}ON)_2,H_2PtCl_6,$$

forms small, orange crystals; when treated successively with methyl iodide, silver and auric chlorides it yields the *platinichloride*,

$$(C_{11}H_{23}ON)_2,H_2PtCl_6,$$

obtained as small crystals.

Methylpropyldiacetonalkamine [*methyl-β-methylpropylaminoisobutylcarbinol*], $OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NMePr^{\alpha}$, similarly prepared by using propyl iodide, is a colourless liquid, b. p. 213—215°; the *aurichloride* is unstable; the *platinichloride*, $2C_{10}H_{23}ON,H_2PtCl_6$, forms small, reddish-yellow crystals, m. p. 195° (decomp.). The *methochloride* gives a *platinichloride*, $(C_{11}H_{25}ON)_2,H_2PtCl_6$, which forms small, red crystals, m. p. 150°.

Benzylmethyldiacetonalkamine [*methyl-β-benzylmethylaminoisobutylcarbinol*], $OH\cdot CHMe\cdot CH_2\cdot CMe_2\cdot NMe\cdot CH_2Ph$, obtained by using benzyl chloride, is a colourless oil, b. p. 169—171°/18 mm.; the *aurichloride* is an oil; the *platinichloride*, $(C_{14}H_{23}ON)_2,H_2PtCl_6$, is a brick-red, crystalline powder decomposing at 197—198°; from the *methiodide*, a solid, white substance, are formed the crystalline *aurichloride*,

$$C_{15}H_{25}ON,HAuCl_4,$$

m. p. 82—84°, and the *platinichloride*, $(C_{15}H_{25}ON)_2,H_2PtCl_6$, a brick-red, crystalline powder decomposing at 167—168°.

Dimethyldiacetonalkamine combines with ethyl iodide when heated in a sealed tube, forming an *ethiodide*, which on treatment with silver chloride is converted into the *ethochloride*; the *platinichloride*,

$$(C_{10}H_{23}ON)_2,H_2PtCl_6,$$

forms small, orange crystals which decompose at 156—158°; the *aurichloride*, $C_{10}H_{23}ON,HAuCl_4$, crystallises in yellow scales, m. p. 88—90°.

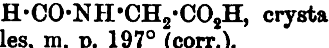
The unsaturated *base*, $C_8H_{17}N$, obtained by treating with strong potassium hydroxide the compound formed by acting on dimethyldiacetonalkamine with hydrogen bromide, is not identical with the *base*, $C_8H_{17}N$, obtained from 1 : 2 : 4 : 4-tetramethyltrimethylenimine (Kohn, this vol., i, 338), although the b. p. 138—140° is the same; the *aurichloride* is an unstable oil; the *platinichloride*, $(C_8H_{17}N)_2,H_2PtCl_6$, forms small, orange-red crystals which decompose at 176°; the *picrate*, $C_{14}H_{20}O_7N_4$, crystallises in long, yellow needles, m. p. 175° (decomp.). With methyl iodide, the unsaturated base forms an *additive* compound, from which is obtained a *platinichloride*, $(C_9H_{19}N)_2,H_2PtCl_6$, crystallising in reddish-yellow needles which decompose at 177°. The methiodide is converted by moist silver oxide into an *ammonium* base, which decomposes when boiled with water into trimethylamine, water, and a hydrocarbon, C_6H_{10}, identical with that obtained by Kohn and Morgenstern (following abstract). W. H. G.

Derivatives of Diacetonalkamines. VIII. Moritz Kohn and Otto Morgenstern (*Monatsh.*, 1907, **28**, 529—536).—With the object of examining the products formed by the oxidation of the hydrocarbon, C_6H_{10}, obtained by Kohn (this vol., i, 328) from 1 : 2 : 2 : 4-tetramethyltrimethylenimine, it has again been prepared by this method, and is found to be identical with the hydrocarbon obtained by the authors from 2 : 4 : 4-trimethyl-1-ethyltrimethylenimine and methylethyldiacetonalkamine, and by Kohn and Schlegl from dimethyldiacetonalkamine (preceding abstracts). Now it has been shown (this vol., i, 628) that the hydrocarbon is probably δ-methyl-$\Delta^{\alpha\gamma}$-pentadiene, $CMe_2{:}CH{\cdot}CH{:}CH_2$; the unsaturated base, through which it is obtained from 2 : 4 : 4-trimethyl-1-ethyltrimethylenimine and methylethyldiacetonalkamine, is therefore in all probability δ-methylethylamino-δ-methyl-Δ^{α}-amylene, $NMeEt{\cdot}CMe_2{\cdot}CH_2{\cdot}CH{:}CH_2$. It was also to be expected that the unsaturated base, $C_8H_{17}N$, obtained from 1 : 2 : 4 : 4-tetramethyltrimethylenimine, would be identical with that obtained from dimethyldiacetonalkamine, namely, *δ-dimethylamino-δ-methyl-Δ^{α}-amylene*, $NMe_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CH{:}CH_2$; but this is not the case (Kohn and Schlegl, preceding abstract). However, although differing from the latter compound, it nevertheless gives rise to the same hydrocarbon, so that it is probably *δ-dimethylamino-β-methyl-Δ^{β}-amylene*, $NMe_2{\cdot}CHMe{\cdot}CH{:}CMe_2$. W. H. G.

Synthesis of Polypeptides. XIX. Emil Fischer (*Annalen*, 1907, **354**, 1—54. Compare this vol., i, 486).—*Derivatives of Phenylalanine.*—[With Paul Blank.]—Polypeptides consisting of combinations of phenylalanine with glycine, alanine, or leucine (compare Abstr., 1904, i, 867, 890) are formed together with cinnamoyl-glycine, -alanine, or -leucine, from α-bromodihydrocinnamic acid, by conversion of this into α-bromopropionyl chloride, action of the chloride on glycine, alanine, or leucine in aqueous sodium hydroxide solution cooled by ice, and treatment of the product with 23% ammonia. The compounds described are inactive, having been prepared from racemic compounds; two stereoisomeric forms of phenylalanyl-leucine have been obtained.

α-Bromo-β-phenylpropionylglycine,

$$CH_2Ph{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

crystallises in microscopic prisms or scales, m. p. 149° (corr.). *i*-Phenylalanylglycine (Abstr., 1905, i, 863) forms a light blue, crystalline *copper* salt, and when treated with hydrogen chloride in alcoholic solution yields the *anhydride*,  $CH_2Ph{\cdot}CH{<}\begin{matrix}CO{\cdot}NH\\NH{\cdot}CO\end{matrix}{>}CH_2$, m. p. 280° (corr. partial decomp.).

Cinnamoylglycine, $CHPh{:}CH{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, crystallises from water in long, colourless needles, m. p. 197° (corr.).

α-Bromo-β-phenylpropionylalanine,

$$CH_2Ph{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,$$

crystallises in long prisms, m. p. 193° (corr. decomp.), and may be a mixture of two isomeric racemides. *Phenylalanylalanine*,

$$CH_2Ph{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H,$$

crystallises in colourless, microscopic needles, m. p. about 241° (corr. decomp.), and forms a *copper* salt crystallising in characteristic, stellate groups of needles and dissolving in water to a cornflower-blue solution.

a-Bromo-β-phenylpropionyl-leucine,

$CH_2Ph\cdot CHBr\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO_2H$,

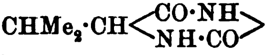
is obtained in two forms, which are separated by treatment with benzene. The isomeride *B* crystallises from benzene in microscopic needles, m. p. 148° (corr.), and yields *phenylalanyl-leucine B*, $CH_2Ph\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO_2H$, crystallising in small prisms, m. p. 224·5° (corr.), with a bitter taste; the *copper* salt crystallises in small prisms. The *propionyl-leucine A* is insoluble in benzene, crystallises from boiling toluene in hexagonal leaflets, m. p. 166·5° (corr.), and yields *phenylalanyl-leucine A*, which crystallises from hot water in needles, m. p. 196°, and has solubilities closely resembling those of its isomeride.

Derivatives of i-*Valine*.—[With JULIUS SCHENKEL.]—Polypeptides containing the group $CHMe_2\cdot CH(NH_2)\cdot CO\cdot$ are prepared from *a*-bromo*iso*valeric acid by the general methods of synthesis previously described. The acid chloride acts readily on *a*-amino-acids, but the subsequent substitution of bromine by the amino-group takes place only at 100° with poor yields, or in some cases does not take place. The action of *a*-bromo*iso*valeryl chloride on *i*-alanine leads to the formation of two racemic isomerides.

*a-Bromo*iso*valeryl chloride*, prepared by the action of thionyl chloride on the acid, is obtained as a transparent, mobile liquid, b. p. 59°/15 mm., crystallises when cooled by liquid air and attacks the mucous membrane.

*a-Bromo*iso*valerylglycine*, $CHMe_2\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, crystallises from water in large prisms, m. p. 139—141° (corr.) evolving gas.

dl-*Valylglycine*, $CHMe_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, crystallises in thin, colourless prisms, m. p. 251° (corr.), is almost tasteless, is only slightly acid to litmus, and forms a *copper* salt crystallising in hexagonal prisms. A small amount of a product which decolorises permanganate in sodium carbonate solution and is probably a glycine derivative of dimethylacrylic acid is formed together with the dipeptide.



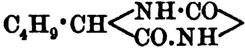
Valylglycine anhydride, $CHMe_2\cdot CH{<}{\scriptstyle\begin{matrix}CO\cdot NH\\ NH\cdot CO\end{matrix}}{>}CH_2$, formed by heating valylglycine over a free flame, crystallises in thin prisms, m. p. 252° (corr.).

*a-Bromo*iso*valerylalanine A*, $C_8H_{14}O_3NBr$, crystallises from hot water in colourless, flat needles, m. p. 165—168° (corr.), and is converted by ammonia into *valylalanine A*, $C_8H_{16}O_3N_2$, which crystallises in small, rhombic leaflets, m. p. 246° (corr.), is almost tasteless, has a slight acid reaction to litmus, and forms a *copper* salt crystallising in blue prisms. *Valylalanine anhydride*, $C_8H_{14}O_2N_2$, formed from valylalanine *A*, crystallises in colourless needles, m. p. 246° (corr.), and is probably a mixture of two isomerides.

*a-Bromo*iso*valerylalanine B*, obtained on evaporating the mother liquors from the *A*-isomeride, crystallises in prisms, m. p. 129—132° (corr.); it is doubtful if this has been obtained free from its isomeride.

i-*Valine anhydride*, $C_{10}H_{18}O_2N_2$, prepared by heating *r*-valine, crystallises in long, colourless needles, m. p. 303° (corr.), and is indifferent to acids or alkalis.

Resolution of Diketopiperazines and Dipeptides of Tyrosine.—[With WALTHER SCHRAUTH.]—The resolution of the diketopiperazines by means of alkalis, which takes place with great ease in the case of glycine anhydride, is hindered by the presence of alkyls, so that it occurs no longer with leucine anhydride (Abstr., 1906, i, 324). This is the case also with valine anhydride, derived from *a*-amino*iso*valeric acid.



The resolution of diketopiperazines derived from mixed dipeptides may lead to the formation of two isomeric dipeptides. This possibility has been studied particularly in the case of *dl*-leucylglycine anhydride, $C_4H_9{\cdot}CH{<}\begin{matrix}NH{\cdot}CO\\ CO.NH\end{matrix}{>}CH_2$, which on hydrolysis is found to yield leucylglycine and glycylleucine in the proportion, 2 : 1. Similar results have been obtained with *i*-leucylalanine anhydride, leucylalanine and alanylleucine being formed in about the proportion 3 : 2.

The resolution of diketopiperazines has been employed now in the preparation of previously unknown derivatives of tyrosine. Hydrolysis of glycyl-*l*-tyrosine anhydride with dilute alkalis at 35° leads to the formation of l-*tyrosylglycine* together with only small amounts of the known isomeride, glycyl-*l*-tyrosine. A substance which is probably *tyrosyltyrosine* is obtained in the same manner from tyrosine anhydride.

Glycyl-*l*-tyrosine anhydride, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{<}\begin{matrix}NH{\cdot}CO\\ CO{\cdot}NH\end{matrix}{>}CH_2$, prepared by the action of ammonia on ethyl chloroacetyl-*l*-tyrosine at 0°, crystallises in needles, m. p. about 295° (corr.), $[a]_D^{20}$ +125·4°, and is probably identical with Fischer and Aberhalden's product from silk-fibroin (Abstr., 1906, i, 718).

l-*Tyrosylglycine* is obtained as a hygroscopic, amorphous mass; the *hydrochloride* of the ethyl ester, $C_{18}H_{18}O_4N_2,HCl$, crystallises in colourless needles, m. p. 230—235° (corr.), $[a]_D^{20}$ +14·1°; the *platinichloride*, $(C_{13}H_{18}O_4N_2)_2,H_2PtCl_6$, m. p. 224—227° (corr. decomp.). The *l*-tyrosylglycine and its derivatives are probably not pure, since the resolution of optically active diketopiperazines is accompanied by partial racemisation (compare Abstr., 1906, i, 145).

Ethyl glycyl-l-*tyrosine platinichloride* crystallises in golden, microscopic plates, and decomposes when heated or boiled with water.

Methyl l-*tyrosine*, $C_{10}H_{13}O_3N$, crystallises in colourless needles, m. p. 135—136° (corr.), $[a]_D^{20}$ +25·75°, and is soluble in alkalis, but not in alkali carbonates. l-*Tyrosine anhydride*, formed by heating the methyl ester in methyl alcoholic solution at 100°, or in the absence of a solvent at 135—140°, crystallises in colourless needles, m. p. 277—280° (corr. decomp.), $[a]_D^{20}$ −223·8°, and gives Millon's reaction. Prolonged heating of the methyl ester leads to partial racemisation, the product containing only 10% of *l*-tyrosine anhydride; the remaining 90% consists of a mixture of the two possible modifications of i-*tyrosine anhydride*, forming needles and stout crystals, m. p. about 300° (corr.). The supposed *tyrosyltyrosine*, obtained in small amount by the hydrolysis of the anhydride with sodium hydroxide, forms an amorphous mass, gives Millon's reaction, and on esterification and treatment with ammonia yields tyrosine anhydride.

Isomeric Leucyl-leucines and their Anhydrides.—[With ARTHUR H. KOELKER.]—Leucyl-leucine has been obtained previously only in one active, the *ll*-, and a racemic form, whereas four active and two racemic modifications are possible theoretically. The missing forms have been prepared now by the general methods described previously (Abstr., 1906, i, 810). *r*-Leucine is resolved by means of its formyl derivative into its optical isomerides (Abstr., 1906, i, 72); one of these is converted by the action of bromine and nitric oxide into the active bromo*iso*hexoic acid, Walden's transformation taking place. The four active leucyl-leucines and the two racemic compounds are formed by combination of the active bromo*iso*hexoic acids with the active leucines.

The *i*-leucyl-leucine previously described is termed leucyl-leucine *A*, and is *d*-leucyl-*l*-leucine + *l*-leucyl-*d*-leucine. It is found now that in the preparation of *i*-bromo*iso*hexoyl-leucine, a small amount of an isomeride is formed, from which the second racemic dipeptide, leucyl-leucine *B* = *d*-leucyl-*d*-leucine + *l*-leucyl-*l*-leucine, is obtained by the action of ammonia.

*l-a-Bromo*iso*hexoyl*-l-*leucine*, $C_{12}H_{22}O_3NBr$, crystallises in thin prisms, m. p. 128° (corr.), $[\alpha]_D^{20}$ $-34{\cdot}97°$ in ethyl acetate, $[\alpha]_D^{20}$ $-53{\cdot}22°$ in *N*/2 sodium hydroxide solution, and gradually decomposes in alkaline solution.

d-*Leucyl*-l-*leucine*, $C_{12}H_{24}O_3N_2$, m. p. 285° (corr.), $[\alpha]_D^{20}$ $-67{\cdot}97°$, and is hygroscopic.

trans-*Leucine anhydride*, $C_{12}H_{22}O_2N_2$, m. p. 287—289° (corr.), is optically inactive.

d-*a-Bromo*iso*hexoyl*-d-*leucine*, $[\alpha]_D^{20}$ $+34{\cdot}70°$ in ethyl acetate, or $[\alpha]_D^{20}$ $+53{\cdot}03°$ in *N*/2 sodium hydroxide solution.

l-*Leucyl*-d-*leucine*, $[\alpha]_D^{20}$ $+68{\cdot}95°$, yields the *trans*-anhydride.

l-*a-Bromo*iso*hexoyl*-d-*leucine* crystallises in small octahedra, $[\alpha]_D^{20}$ $-15{\cdot}82°$.

d-*Leucyl*-d-*leucine* crystallises from alcohol, $[\alpha]_D^{20}$ $+13{\cdot}16°$ in *N*-sodium hydroxide.

d-*Leucine anydride*, $[\alpha]_D^{20}$ $+46{\cdot}02$—$48{\cdot}67°$.

i-*a-Bromo*iso*hexoyl-leucine B* crystallises from ether in thin prisms, m. p. 120—121° (corr.).

i-*Leucyl-leucine B* crystallises in small leaflets, m. p. 267—268° (corr. decomp.); the *hydrochloride* and *nitrate* form small prisms; the *copper* salt is crystalline.

The action of *i-a*-bromo*iso*hexoic acid on *l*-leucine leads to the formation of a mixture of *d-a*-bromo*iso*hexoyl-*l*-leucine and *l-a*-bromo*iso*hexoyl-*l*-leucine; the former is separated by solution of the mixture in ethyl acetate and addition of light petroleum. The *ll*-isomeride is purified by conversion into the dipeptide and recrystallisation of this from alcohol.

The rate of hydrolysis of *d*-leucyl-*l*-leucine by 10% hydrochloric acid at 99—100° has been determined, and the results are expressed in a curve.

G. Y.

Formation of Calcium Cyanamide and of Calcium Carbide. E. Rudolfi (*Zeitsch. anorg. Chem.*, 1907, **54**, 170—184. Compare Kühling, this vol., ii, 166; Bredig, this vol., i, 396).—The conditions under which calcium cyanamide is formed from calcium carbide and nitrogen and directly from its components have been investigated.

When commercial carbide, containing 82% of the pure substance, is heated in a porcelain tube in an electric furnace and nitrogen (dry or moist) passed over it, no appreciable amount of cyanamide is formed below 700°; beyond this point the amount of nitrogen absorbed increases regularly with the temperature and duration of the experiment. The rate of reaction is greatly increased by the addition of calcium chloride, but only when the temperature is sufficiently high to fuse the salt. Dry nitrogen gives rather better results than the moist gas.

The experiments on the formation of cyanamide from carbon, calcium oxide, and nitrogen were carried out in a charcoal tube immersed in an electric furnace, the temperatures being measured with an optical pyrometer. It was first shown that calcium carbide is formed from the oxide and nitrogen only when the temperature is raised to 1800—1819°, the temperature for this equilibrium (under a partial pressure of 1/5 atmosphere carbon monoxide) found by Rothmund (Abstr., 1902, ii, 454) being much too low. When the oxide and carbon were heated in nitrogen, cyanamide and carbide were both formed at 1738—1753°, but neither could be detected at lower temperatures. It is therefore considered that the formation of calcium carbide precedes that of cyanamide; the fact that the equilibrium temperature is rather lower in the latter series of experiments is due in all probability to the much smaller pressure of carbon monoxide. The equilibrium temperature is in fair agreement with that calculated by Nernst's formula connecting equilibrium and temperature.

When calcium cyanamide is heated in a current of carbon monoxide it is partially reduced to carbide; this reaction is being investigated further. G. S.

Halogen Compounds of Molybdenum and Tungsten. Arthur Rosenheim (*Zeitsch. anorg. Chem.*, 1907, **54**, 97—103. Compare Abstr., 1905, ii, 717; 1906, i, 603).—The compound previously obtained by the action of excess of potassium cyanide on the compound $Mo(OH)_2(SCN)_3,2C_5H_5N$ is now shown to have the formula $K_4Mo(CN)_8,2H_2O$ ascribed to it by its discoverer, Chilesotti (Abstr., 1905, i, 177), and not that formerly suggested by Rosenheim and Koss (*loc. cit.*). By titration with potassium permanganate, however, it is shown that, contrary to the view of Chilesotti, it is a compound of *quinquevalent* molybdenum, and it has so far been found impossible to determine its constitution. Electrical conductivity measurements appear to show that it has the simple formula in solution, and cryoscopic determinations have not thrown much light on the subject.

The compound is readily soluble in water, and is stable towards acids and dilute alkalis. By double decomposition in aqueous solution, many other salts of the same acid have been prepared, but only the following have been fully investigated. The *thallium* salt, $Tl_4Mo(CN)_8$, occurs in long, lustrous, reddish-yellow needles, slightly soluble in water. The *cadmium* salt, $Cd_2Mo(CN)_8,8H_2O$, forms light yellow, microscopic needles, insoluble in water. From the solution of the last-named salt in boiling concentrated ammonia, the *cadmium ammine*, $Cd_2(NH_3)_4Mo(CN)_8,2H_2O$, was obtained in deep yellow needles on cooling. The corresponding *copper ammine*, $Cu_2(NH_3)_4Mo(CN)_8,7H_2O$, has also been obtained; it occurs in deep green needles.

The crystallographic characters of the potassium and thallium salts are given. G. S.

Double Platinocyanides of Calcium, Strontium, and Barium, &c. HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1907, 43, 356—368). —Crystallographic descriptions are given of the following salts: $Pt(CN)_4Ca,5H_2O$; $Pt(CN)_4Sr,5H_2O$; $Pt(CN)_4Ba,5H_2O$; $Pt(CN)_4NaK,3H_2O$; $Pt(CN)_4Mg,7H_2O$; $Pt(CN)_4Y_{\frac{2}{3}},7H_2O$.

L. J. S.

Some New Platinocyanides. LEONARD A. LEVY (*Proc. Camb. Phil. Soc.*, 1907, 14, 159—160).—In continuation of the investigation on the platinocyanides of hydrazine and hydroxylamine (Levy and Sisson, Trans., 1906, 89, 125), the following salts have been prepared.

Guanidine platinocyanide, $(CH_5N_3)_2,H_2Pt(CN)_4$, prepared by the interaction of guanidine carbonate and barium platinocyanide, forms long, silky, white needles.

1 : 4-*Diphenyl*-3 : 5-endo-*anilo*-4 : 5-*dihydro*-1 : 2 : 4-*triazole* (*nitron*) *platinocyanide*, $(C_{20}H_{16}N_4)_2Pt(CN)_4$, prepared by adding an aqueous solution of hydroplatinocyanic acid to an acetic acid solution of nitron, crystallises in shining grey plates.

Uranyl platinocyanide, prepared by double decomposition between uranyl sulphate and barium platinocyanide, separates from its aqueous solution at the ordinary temperature as red crystals with strong green metallic reflexion; imperfect, yellow crystals are obtained by evaporating the solution on a water-bath, which become reddish-green when cooled. The two forms probably represent different degrees of hydration. The reddish-green form changes into the yellow form at 39°.

W. H. G.

Dimagnesium Derivative of $\alpha\epsilon$-Dibromopentane. VICTOR GRIGNARD and G. VIGNON (*Compt. rend.*, 1907, 144, 1358—1360).— $\alpha\epsilon$-Dibromopentane, prepared by von Braun's method (Abstr., 1904, i, 841), reacts readily with magnesium, in presence of ether, forming a mobile, slightly coloured *dimagnesium* derivative. On treatment with carbon dioxide, this is converted into *cyclo*hexanone, pimelic acid, and probably *decamethylenedicarboxylic acid*, brilliant cottony flocks, m. p. 124—125°. Ethyl acetate reacts with the dimagnesium derivative, forming *tert.*-methyl*cyclo*hexanol and a *hydrocarbon*, b. p. 70—110°, which may be methyl*cyclo*hexene produced by dehydration of the alcohol. Diacetyl reacts with the dimagnesium derivative, forming a viscous, yellow liquid, b. p. 122—126°/14 mm., with an unpleasant butyric odour, which may be *dimethylcycloheptanediol*. The corresponding *diacetate* boils at 129—131°/12 mm. T. A. H.

The Four Dinitro-derivatives of *o*-Dibromobenzene. GEORG KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 843—846).—1 : 2-Dibromo-4 : 5-dinitrobenzene, prepared by Schiff (Abstr., 1891, 44), crystallises in the rhombic, bipyramidal class of the trimetric system [ARTINI. $a:b:c=0\cdot7085:1:0\cdot4961$].

1 : 2-Dibromo-3 : 5-dinitrobenzene (Schiff, *loc. cit.*) forms crystals belonging to the prismatic class of the monoclinic system [ARTINI. $a:b:c=0\cdot8708:1:0\cdot5683$; $\beta=89°32'$].

When 1 : 2-dibromo-3-nitrobenzene is nitrated with a mixture of nitric and sulphuric acids, it yields: (1) 1 : 2-dibromo-3 : 5-dinitrobenzene; (2) 1 : 2-*dibromo*-3 : 4-*dinitrobenzene*, $C_6H_2Br_2(NO_2)_2$, which separates from ethyl acetoacetate or carbon disulphide in faintly green, prismatic crystals, m. p. 109°, belonging to the prismatic class of the monoclinic system (ARTINI. $a:b:c=0\cdot5717:1:0\cdot6912$; $\beta=63°41'$]; (3) 1 : 2-*dibromo*-3 : 6-*dinitrobenzene*, $C_6H_2Br_2(NO_2)_2$, which crystallises from carbon disulphide in almost white scales, or from a mixture of alcohol and ether in prisms or plates, m. p. 156·4°, belonging to the prismatic class of the monoclinic system [ARTINI. $a:b:c=1\cdot7263:1:1\cdot4846$]. T. H. P.

Electrolytic Reduction of *p*-Toluenesulphonyl Chloride. FRITZ FICHTER and W. BERNOULLI (*Zeitsch. Elektrochem.*, 1907, **13**, 310—312).—When a solution of *p*-toluenesulphonyl chloride in 2*N*-alcoholic hydrogen chloride is electrolysed, the main product is the corresponding sulphinic acid, which is partly converted into the ethyl ester and partly decomposes, thus:

$$3C_6H_4Me\cdot SO_2H=C_6H_4Me\cdot SO_2\cdot S\cdot C_6H_4Me+C_6H_4Me\cdot SO_3H+H_2O.$$

In presence of titanium trichloride and using a nickel gauze cathode the main product is *p*-tolyl mercaptan. The same result is obtained by reducing a suspension of the sulphonyl chloride in aqueous sulphuric acid at 80° with a lead cathode. The best method, however, is to use a saturated solution of *p*-toluenesulphonyl chloride in 2*N*-alcoholic sulphuric acid to which a quantity of the solid substance is added, this is stirred rapidly in a porous cell by means of a lead cathode. A water-cooled coil of lead tubing serves as anode; a cathodic current density of 0·13 ampere per sq. cm. gives a good yield of the mercaptan. T. E.

Ditolane Hexachloride. WILLY MARCKWALD and L. KARCZAG (*Ber.*, 1907, **40**, 2994—2996. Compare Wislicenus and Blank, Abstr., 1889, 261; Löb, Abstr., 1903, i, 811).—The authors have repeated Wislicenus and Blank's work and confirm their results, except that they find the supposed ditolane hexachloride to be an isomorphous mixture of tolane tetrachloride and *a*-tolane dichloride. The formation of the isomorphous mixture on prolonged fusion of the tetrachloride with *β*-tolane dichloride results from transformation of the *β*- into the *a*-dichloride on prolonged heating. *a*-Tolane dichloride has m. p. 150°; tolane tetrachloride, m. p. 161·5°. The graph representing the m. p. of mixtures of these substances is a straight line; the molecular mixture, m. p. 156°; the mixture obtained by partial reduction of tolane tetrachloride melts at a lower temperature in consequence of containing a slight excess of the dichloride. G. Y.

Triphenylmethyl. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1907, 40, 3056—3058).—A reply to Gomberg (this vol., i, 504). C. S.

Dibenzylideneacetone and Triphenylmethane. IX. ADOLF VON BAEYER (*Ber.*, 1907, 40, 3083—3090).—Largely a criticism of the quinonoid theory of coloured salts derived from triphenylcarbinol, &c. (compare Gomberg, this vol., i, 504). The salts formed by the union of ferric chloride with the halogen derivatives of tri-*p*-chloro- (bromo-, iodo-) triphenylmethane have been prepared, and the decomposing effect of alkali or water in the presence of acetone examined. In all cases it was found that the halogen acid liberated was that derived from the ferric chloride and the carbinol haloid; no trace of the removal of the nucleus halogen atoms could be detected.

[With HANS AICKELIN.]—*Tri*-p-*chlorotriphenylmethyl bromide*,

$$C(C_6H_4Cl)_3Br,$$

froms long, colourless needles, m. p. 148°. *Tri*-p-*bromotriphenylmethyl chloride ferrichloride*, $C_{19}H_{12}Cl_4Br_3Fe$, forms a brick-red, crystalline powder, m. p. 237°.

Tri-p-*chlorotriphenylmethyl bromide ferrichloride*, $C_{19}H_{12}Cl_6BrFe$, forms brown plates with a bluish-green lustre, m. p. 217°.

Tri-p-*iodotriphenylmethyl chloride ferrichloride*, $C_{19}H_{12}Cl_4I_3Fe$, forms olive-green crystals, which when rubbed yield a red powder.

Tri-p-*chlorotriphenylmethyl bromide ferribromide*, $C_{19}H_{12}Cl_3Br_4Fe$, forms brownish-green prisms and plates, m. p. 216°.

According to Gomberg's formulæ, the two compounds,

$$C(C_6H_4Cl)_3Br,FeCl_3 \text{ and } C(C_6H_4Br)_3Cl,FeCl_3,$$

should behave similarly towards water or alkali as the quinonoid grouping is the same, but it is shown that the former yields 1Br and 3Cl, and the latter, 4Cl. J. J. S.

Hexahydrophenylglycine. NICOLAI D. ZELINSKY and B. ARZIBACHEFF (*Ber.*, 1907, 40, 3053—3055. Compare Zelinsky and Stadnikoff, this vol., i, 425).—*Hexahydrophenylglycine* (cyclo*hexylglycine*), $C_6H_{11}\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 227—228° (decomp.), is obtained by the hydrolysis of the *nitrile*; this results from the interaction of *cyclo*hexylamine hydrochloride, 40% formaldehyde, and concentrated aqueous potassium cyanide in the cold, and is isolated from absolute ether in the form of the *hydrochloride*, $C_6H_{11}\cdot NH\cdot CH_2\cdot CN,HCl$, m. p. 193—194° (decomp.). The acid forms a vivid blue *copper* salt, $C_{16}H_{24}O_4N_2Cu,H_2O$, and a *nitroso*-compound, $C_6H_{11}\cdot N(NO)\cdot CH_2\cdot CO_2H$, m. p. 117·5—118°. C. S.

Constitution of Xanthoxanil. SIEGFRIED RUHEMANN (*Ber.*, 1907, 40, 3015—3017).—A reply to Wohl and Freund (*ibid.*, 2304), who suggest a formula for xanthoxanil different from the author's (Trans., 1906, **89**, 1236—1847). A. McK.

Preparation of the Aniline Derivatives of Succinic Acid and of Phthalic Acid. J. BISHOP TINGLE and MARSHALL P. CRAM (*Amer. Chem. J.*, 1907, **37**, 596—604).—An account is given of improved methods for preparing succinanil, succinanilic acid, succinanilide, phthalanil, and phthalanilic acid. Phthalanilide is best prepared by the method of Rogoff (Abstr., 1897, i, 470). E. G.

Substituted Bromoanilines. J. R. HILL (*Proc. Camb. Phil. Soc.*, 1907, **14**, 166—170).—The following compounds, obtained by acting on the corresponding tertiary aniline in glacial acetic acid with bromine, were prepared with the object of obtaining, by the addition of allyl or benzyl iodide, two series of substituted ammonium compounds containing an asymmetric nitrogen atom. These compounds, since they contain a brominated phenyl group, would differ in this respect from those investigated by Thomas and Jones (Trans., 1906, **89**, 280), and hence admit of the study of the effect produced on the optical activity by the introduction of the bromine atom into the phenyl group.

Only in the case of the methylethylbromoaniline has it been possible to determine the position of the bromine atom. The quaternary hydroxide obtained from the methiodide of this compound gave on distillation *p*-bromodimethylaniline; the other quaternary hydroxides on distillation gave back the original bromoaniline. None of the methiodides of these compounds are decomposed by strong potassium hydroxide solutions.

p-Bromomethylethylaniline is an oil, b. p. 149—152°/13 mm. (compare Claus and Howitz, Abstr., 1884, 1005); the *methiodide*, m. p. 189°, and *picrate*, m. p. 138°, are both crystalline substances. The base combines with allyl iodide, yielding p-*bromophenylmethylethylallylammonium iodide*, which forms crystals, m. p. 134°.

*Methyl*iso*propylbromoaniline*, $NMePr^{\beta}\cdot C_6H_4Br$, crystallises in lustrous plates, m. p. 34°; the *hydrobromide*, m. p. 69°, *methiodide*, m. p. 167°, and *picrate*, m. p. 138°, are crystalline compounds; with allyl iodide is obtained *bromophenylmethyl*iso*propylallylammonium iodide*, $C_{13}H_{19}NBrI$, a crystalline substance, m. p. 150°.

Methylpropylbromoaniline, $C_{10}H_{14}NBr$, is an oil, b. p. 149—152°/5 mm.; the *methiodide*, m. p. 167°, and *picrate*, m. p. 126°, form well-defined crystals.

*Methyl*iso*butylbromoaniline*, $C_{11}H_{16}NBr$, is an oil, b. p. 169—173/9 mm.; the *methiodide*, m. p. 167—168°, and *picrate*, m. p. 136—137°, are readily obtained in a crystalline form.

*Methyl*iso*amylbromoaniline*, $C_{12}H_{18}NBr$, is an oil, b. p. 165—170°/5 mm; the *methiodide*, m. p. 176°, and *picrate*, m. p. 89°, are crystalline substances. W. H. G.

Resolution of Salts of Asymmetric Nitrogen Compounds and Weak Organic Acids. MISS ANNIE HOMER (*Proc. Camb. Phil. Soc.*, 1907, **14**, 196—198).—Inactive phenylbenzylmethyl*iso*propylammonium hydroxide may be resolved by repeated crystallisation of the d-*hydrogen tartrate*, $(C_{17}H_{22}N)C_4H_5O_6,H_2O$. Attempts were therefore made to resolve inactive mixtures of *d*- and *l*-mandelic acids and of *d*- and *l*-valeric acids by means of active phenylbenzylmethyl*iso*propylammonium iodide (Thomas and Jones, Trans., 1906, **89**, 280), but a complete resolution could not be effected, owing to the fact that the solutions, being dilute, have to remain for some considerable time before crystallisation takes place and hence racemisation occurs during the process. If a concentrated solution of the active ammonium hydroxide could be obtained, it is probable that a complete resolution might be effected. W. H. G.

Derivatives of Diacetonalkamine. IX. Moritz Kohn (*Monatsh.*, 1907, **28**, 537—541).—Diacetonalkamine and benzyl chloride do not react together at the ordinary temperature, but when heated together a violent reaction takes place with the formation of *benzyldiacetonalkamine* [*methyl-β-benzylamino*iso*butylcarbinol*],

$$CH_2Ph{\cdot}NH{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH,$$

and tribenzylamine. This latter compound is undoubtedly produced by the interaction of benzyl chloride with ammonia formed by the decomposition of the diacetonalkamine during the violent reaction.

Benzyldiacetonalkamine forms a colourless oil, b. p. 164—165°/15mm.; the *aurichloride*, $C_{13}H_{21}ON,HAuCl_4$, crystallises in glittering scales, m. p. 157—160°; the *platinichloride*, $(C_{13}H_{21}ON)_2,H_2PtCl_6$, is crystalline. The *nitroso*-derivative, $C_{13}H_{20}O_2N_2$, crystallises from light petroleum in thin needles, m. p. 48°. W. H. G.

Aromatic Dithiocarbamates. II. Sima M. Losanitsch (*Ber.*, 1907, **40**, 2970—2977).—The product obtained from the action of carbon disulphide on amines depends on the basicity of the amine. Thus, whilst ammonia and primary or secondary aliphatic amines form dithiocarbamates, aromatic amines, in general, yield thiocarbamides. On the other hand, it has been found (Abstr., 1892, 55; Delepine, Abstr., 1902, i. 702) that in the presence of ammonia, primary and secondary aromatic amines form ammonium dithiocarbamates. The present work was undertaken to determine which aromatic amines are capable of forming dithiocarbamates directly, and which only with the assistance of a stronger base; the constitution of the dithiocarbamates formed by the action of carbon disulphide on two amines also has been determined.

Aniline, *p*-toluidine, *a*- and *β*-naphthylamines, *o*-, *m*-, and *p*-phenylenediamines, *m*-tolylenediamine, benzidine, and *o*-tolidine form dithiocarbamates only in the presence of ammonia, or, in some cases, of phenylhydrazine or piperidine. This influence of ammonia, phenylhydrazine, and piperidene diminishes in the order in which these substances are named: thus benzidine in presence of ammonia forms a bisdithiocarbamate, but only a monodithiocarbamate with the assistance of phenylhydrazine, whilst it does not react with carbon disulphide in presence of piperidine. In the product, $NR'R''{\cdot}CS{\cdot}SH,NHR_2$, formed by the action of carbon disulphide on a mixture of amines, the group NR′R″ is derived from the weaker base; hence an amine may function differently as it reacts in presence of a stronger or a more feeble base. Thus phenylhydrazine forms *ammonium anilinodithiocarbamate*, $NHPh\cdot NH\cdot CS\cdot SNH_4$, but *phenylhydrazonium phenyldithiocarbamate*, $NHPh\cdot CS\cdot SH,NH_2\cdot NHPh$, in presence of ammonium and aniline respectively. Similarly, piperidine forms *ammonium piperylenedithiocarbamate*, $C_5H_{10}N\cdot CS\cdot SNH_4$, and *piperidonium phenyldithiocarbamate*, $NHPh\cdot CS\cdot SH,C_5H_{10}N$.

Ammonium aryldithiocarbamates are yellow, crystalline salts which yield diarylthiocarbamides, ammonia, ammonium sulphide, carbon disulphide, and an odour of thiocarbimide when heated. The phenylhydrazonium and piperidonium salts are white, crystalline substances, and are more stable than the ammonium salts.

Halogen, hydroxy-, and nitro-derivatives of aniline, toluidine, and naphthylamine, as also mono-, di-, and tri-aminoazobenzenes, diazoaminobenzene, triphenylguanidine, diphenylamine, and pyrrole do not form dithiocarbamates with carbon disulphide alone or in presence of ammonia, phenylhydrazine, or piperidine.

The following dithiocarbamates are described:

$$NH_2\cdot C_6H_4\cdot NH\cdot CS\cdot S\cdot NH_4,$$

from *o*-phenylenediamine and ammonia, decomposes when heated yielding a product, m. p. 260°; from *m*-phenylenediamine and ammonia, m. p. 90°; from *p*-phenylenediamine, decomposes when heated yielding a product, m. p. 250°. $NH_2\cdot C_6H_3Me\cdot NH\cdot CS\cdot S\cdot NH_4$, from *m*-tolylenediamine, m. p. 100°, decomposes when heated above its m. p.

$$(C_6H_4)_2(NH\cdot CS\cdot S\cdot NH_4)_2,$$

from benzidine and ammonia, m. p. 240° after decomposing and resolidifying. $(C_6H_3Me)_2(NH\cdot CS\cdot S\cdot NH_4)_2$, from *o*-tolidine, m. p. 116° (decomp.). $C_5H_{10}N\cdot CS\cdot S\cdot NH_4$, from piperidine and ammonia, decomposes at 130°. $NHPh\cdot CS\cdot S\cdot NH_3\cdot NHPh$, from aniline and phenylhydrazine, needles, m. p. 82° (compare Busch and Ridder, Abstr., 1897, i, 343).

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot CS\cdot S\cdot NH_3\cdot NHPh,$$

from benzidine and phenylhydrazine, m. p. 120° (decomp.), and when further heated resolidifies, m. p. 189°. $C_5H_{10}N\cdot CS\cdot S\cdot NH_3\cdot NHPh$, from piperidine and phenylhydrazine, m. p. 128°.

$$NH_2\cdot C_6H_4\cdot NH\cdot CS\cdot S\cdot NH_3\cdot NHPh,$$

from *p*-phenylenediamine and phenylhydrazine, colourless needles, m. p. 109°. A *dithiocarbamate*, m. p. 122°, is obtained from phenylhydrazine, tetrahydroquinoline, and carbon disulphide. $NHPh\cdot CS\cdot S\cdot C_5H_{11}N$, from piperidine and aniline, leaflets, m. p. 97°, yields phenylthiocarbimide when boiled with water. $NH_2\cdot C_6H_4\cdot CS\cdot S\cdot C_5H_{11}N$, from piperidine and *p*-phenylenediamine, colourless crystals, m.p. 114—115°.

The action of carbon disulphide on aniline and tetramethylammonium hydroxide leads to the formation of a mixture of diphenylthiocarbamide and *tetramethylammonium phenylcarbamate*; the two substances crystallise together in needles, m. p. 150°, which decompose at the ordinary temperature, forming phenylthiocarbimide, yield diphenylthiocarbamide and phenylthiocarbimide when boiled with water or treated with acids, and dissolve in aqueous alkalis, forming a yellow solution and depositing diphenylthiocarbamide. G. Y.

Bivalency of Glucinum. Glucinum Picrate. BORIS GLASSMANN (*Ber.*, 1907, **40**, 3059—3060).—*Glucinum picrate*, $Gl(C_6H_2O_7N_3)_2,3H_2O$, is obtained by neutralising a warm, aqueous solution of picric acid with glucinum carbonate. The molecular weight of the anhydrous picrate, determined by the cryoscopic method in acetophenone, is 465. The presence of moisture in the solvent causes an elevation of the freezing point, due probably to the hydration of the picrate. C. S.

Nitration of Derivatives of *p*-Aminophenol. FRÉDÉRIC REVERDIN [and FRITZ DINNER] (*Ber.*, 1907, **40**, 2848—2857; *Bull. Soc. Chim.*, [iv], 1, 624. Compare Abstr., 1905, i, 54, 430; 1906, i, 165, 748; this vol., i, 37).—This is a study of the nitration, under varying conditions, of derivatives of *p*-aminophenol in which the hydroxylic and an amino-hydrogen atom are substituted by *p*-toluenesulphonyl and acetyl or benzoyl.

4-p-*Toluenesulphonylaminophenyl acetate*,

$$OAc\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_7H_7,$$

prepared from acetic anhydride and 4-*p*-toluenesulphonylaminophenol, crystallises in rose-coloured leaflets, m. p. 138—139°, and is hydrolysed by cold dilute alkalis, hot aqueous sodium carbonate, or concentrated sulphuric acid.

4-p-*Toluenesulphonylaminophenyl benzoate*, $C_{20}H_{17}O_4NS$, crystallises in needles, m. p. 170°.

From 4-aminophenyl *p*-toluenesulphonate are prepared the *N*-acetyl, m. p. 146°, and the N-*benzoyl* derivative,

$$NHBz\cdot C_6H_4\cdot O\cdot SO_2\cdot C_7H_7,$$

white needles, m. p. 218°.

3 : 5-*Dinitro*-4-p-*toluenesulphonylaminophenol*,

$$C_7H_7\cdot SO_2\cdot NH\cdot C_6H_2(NO_2)_2\cdot OH,$$

crystallising in needles, m. p. 157—158°, is formed by the action of nitric acid, D 1·52, on the acetate at − 10—0°, and, on hydrolysis with concentrated sulphuric acid on the water-bath, yields 3 : 5-dinitro-4-aminophenol. The action of a mixture consisting of 45% of nitric acid, D 1·4, and 55% of concentrated sulphuric acid on the acetate in acetic anhydride solution leads to the formation of a *substance* crystallising from alcohol in white needles, m. p. 145—146°, which contains only 4·81% of nitrogen; 3 : 5-dinitro- and small amounts of 3-nitro-4-aminophenol are obtained on hydrolysis of the mother liquors from this, or of the product of the action of nitric acid, D 1·52, on the acetate in acetic anhydride solution.

Nitration of the benzoate with nitric acid leads to the formation of *nitro*-p-*toluenesulphonyl*-4-*amino*-3 : 5-*dinitrophenylnitrobenzoate*, $NO_2\cdot C_7H_6\cdot SO_2\cdot NH\cdot C_6H_2(NO_2)_2\cdot O\cdot CO\cdot C_6H_4\cdot NO_2$, yellow needles, m. p. 189—190°, or with a mixture of nitric and sulphuric acids in acetic anhydride solution to the formation of a *product* which, on hydrolysis, yields 3-nitro-4-aminophenol.

Nitration of 4-acetylaminophenyl *p*-toluenesulphonate with nitric acid, D 1·4, leads to the formation of 3-*nitro*-4-*acetylaminophenyl nitro*-p-*toluenesulphonate*, $NHAc\cdot C_6H_3(NO_2)\cdot O\cdot SO_2\cdot C_6H_3Me\cdot NO_2$, yellow leaflets, m. p. 146°, or with a mixture of nitric acid, D 1·4, and sulphuric acid in acetic anhydride solution, to the formation of ***3-nitro-4-acetylaminophenyl*** ***p-toluenesulphonate***, $C_{15}H_{14}O_6N_2S$, yellow leaflets, m. p. 134°, or with a mixture of nitric acid, D 1·52, and sulphuric acid in acetic anhydride solution, to the formation of a ***product***, which, on hydrolysis, yields 3-nitro 4-aminophenol. The mononitro-derivative, m. p. 134°, is formed also by the action of acetyl nitrate on 4-acetylaminophenyl *p*-toluenesulphonate in acetic anhydride solution. The introduction of a second nitro-group into the phenol nucleus takes place to only a small extent when the dinitro derivative, m. p. 146°, is treated with nitric acid, D 1·52.

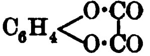
Nitration of 4-benzoylaminophenyl *p*-toluenesulphonate by means of nitric acid, D 1·52, or of a mixture of nitric and sulphuric acids, leads to the formation of a ***trinitro***-derivative, m. p. 145—150°, which, on hydrolysis, yields 3-nitro-4-aminophenol and nitrotoluenesulphonic and *m*-nitrobenzoic acids. This trinitro derivative is formed also to a small extent on nitration of the *N*-benzoyl compound with the acid mixture in acetic anhydride solution, whilst nitration with acetyl nitrate leads to the formation of a ***product*** which, on hydrolysis, yields a mixture of nitro- and dinitro-aminophenols. A small amount of dinitroaminophenol is formed further by hydrolysis of the ***product*** of the action of nitric acid, D 1·52, on the trinitro-compound.

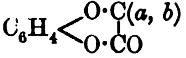
The iodo-acid, m. p. 114—115°, derived from dinitrophenoxyacetic acid (Reverdin and Bucky, Abstr., 1906, i, 748), is found now to be 4-iodo-2 : 5-dinitrophenol, whilst the product, m. p. 201—202°, is 4-iodo-2 : 5-dinitrophenoxyacetic acid. G. Y.

Action of Nitric Acid on Phenol Ethers. HERMANN THOMS and ADOLF SCHÜLER (*Arch. Pharm.*, 1907, **245**, 284—286).

—Examples are tabulated which show that: (1) dimethoxybenzenes all yield nitro-derivatives readily; (2) as the methoxy-groups accumulate, the entry of nitro-groups is retarded, only taking place when a para-position is free, and oxidation to a quinone is favoured; (3) alkyl (propyl) groups favour the entry of nitro-groups, which may take place in a para-position to the alkyl group even when this must be accompanied by elimination of methoxyl from the position in question. C. F. B.

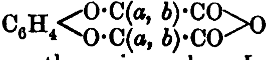
Preparation of Cyclic Esters and Ethers of Catechol. CARL A. BISCHOFF and EMANUEL FRÖHLICH (*Ber.*, 1907, **40**, 2779—2790).

—Whilst oxalic esters of the type  $C_6H_4{<}\begin{array}{l}O\cdot CO\\ \;\;\;\;\;| \\ O\cdot CO\end{array}$ were obtained from each of the dihydroxybenzenes (Bischoff and von Hedenström, Abstr., 1903, i, 27), lactones of the type



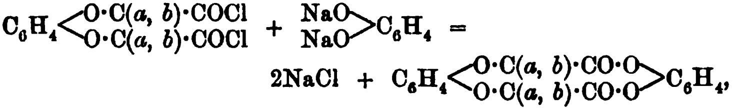
$$C_6H_4{<}\begin{array}{l}O\cdot C(a,\,b)\\ \;\;\;\;\;| \\ O\cdot CO\end{array}$$

were obtained from catechol only; the anhydride type



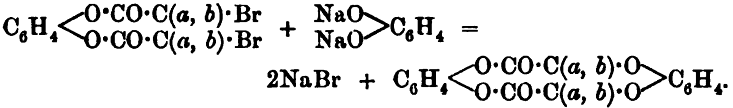
$$C_6H_4{<}\begin{array}{l}O\cdot C(a,\,b)\cdot CO\\ O\cdot C(a,\,b)\cdot CO\end{array}{>}O$$

was represented in the ortho-series only. In the present communication the influences of the ortho-, meta-, and para-positions of the hydroxyl group, on the one hand, and of the groups *a* and *b* (H, Me, Et, and Pr^β), on the other, on the formation of lactones and bis-esters respectively have been examined. The latter esters can be formed from acid chlorides, thus:

(*A*) 

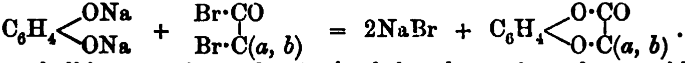
$$C_6H_4<\begin{matrix}O\cdot C(a,b)\cdot COCl\\ O\cdot C(a,b)\cdot COCl\end{matrix} + \begin{matrix}NaO\\ NaO\end{matrix}>C_6H_4 = 2NaCl + C_6H_4<\begin{matrix}O\cdot C(a,b)\cdot CO\cdot O\\ O\cdot C(a,b)\cdot CO\cdot O\end{matrix}>C_6H_4,$$

or thus:

(*B*) 

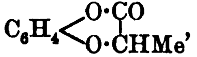
$$C_6H_4<\begin{matrix}O\cdot CO\cdot C(a,b)\cdot Br\\ O\cdot CO\cdot C(a,b)\cdot Br\end{matrix} + \begin{matrix}NaO\\ NaO\end{matrix}>C_6H_4 = 2NaBr + C_6H_4<\begin{matrix}O\cdot CO\cdot C(a,b)\cdot O\\ O\cdot CO\cdot C(a,b)\cdot O\end{matrix}>C_6H_4.$$

Lactones are formed, thus:

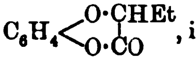
(*C*) 

$$C_6H_4<\begin{matrix}ONa\\ ONa\end{matrix} + \begin{matrix}Br\cdot CO\\ Br\cdot C(a,b)\end{matrix} = 2NaBr + C_6H_4<\begin{matrix}O\cdot CO\\ O\cdot C(a,b)\end{matrix}.$$

Catecholbisoxyacetic acid, obtained by the action of monochloroacetic acid on catechol, has m. p. 177—178°. The *chloride*, $C_6H_4(O\cdot CH_2\cdot COCl)_2$, obtained by the action of thionyl chloride on the acid, has b. p. 213°/41 mm., and separates from a mixture of benzene and light petroleum in crystals, m. p. 49—50°. The cyclic compound, obtained by the action of the chloride on disodium catechol in accordance with *A*, was a resin, which began to crystallise in prisms after several months, but could not be recrystallised; it was not analysed.

Catechol-α-oxypropionyl lactone,  $C_6H_4<\begin{matrix}O\cdot CO\\ O\cdot CHMe\end{matrix}$, was obtained from disodium catechol and ethyl α-bromopropionate.

[With H. HOFFMANN.]—*Bis-a-bromopropionylcatechol*, $C_6H_4(O\cdot CO\cdot CHBrMe)_2$, obtained from disodium catechol and α-bromopropionyl bromide separates from alcohol in colourless leaflets, m. p. 62°.

Bis-a-bromobutyrylcatechol, $C_6H_4(O\cdot CO\cdot CHBrEt)_2$, obtained from disodium catechol (1 mol.) and bromobutyryl bromide (2 mols.), separates from alcohol in colourless leaflets, m. p. 75—76°. If molecular proportions of the sodium compound and the acid bromide are used, *catechol-mono-a-oxybutyrolactone*,  $C_6H_4<\begin{matrix}O\cdot CHEt\\ O\cdot CO\end{matrix}$, is formed as a reddish-yellow oil, b. p. 131°/25 mm.

*Bis-a-bromo*iso*butyrylcatechol*, $C_6H_4(O\cdot CO\cdot CBrMe_2)_2$, prepared from disodium catechol (1 mol.) and bromo*iso*butyryl bromide (2 mols.), is an oil with b. p. 195—200°/20 mm. When molecular proportions of sodium compound and acid bromide are used, the main product is catechol α-oxy*iso*butyrolactone.

*Bis-a-bromo*iso*valerylcatechol*, $C_{16}H_{20}O_4Br_2$, is a colourless oil, b. p. 220—225°/20 mm. *Catecholoxy*iso*valerolactone*, $C_{11}H_{12}O_3$, is a colourless oil, b. p. 128°/20 mm.

A. McK.

Resorcinol and Quinol Esters of Halogenated Fatty Acids.

CARL A. BISCHOFF and EMANUEL FRÖHLICH (*Ber*, 1907, 40, 2790—2803. Compare preceding abstract).—The authors describe representatives of the type $C_6H_4[O\cdot CO\cdot C(a, b)Br]_2$, and also reactions undergone by the compound $C_6H_4\cdot(O\cdot CH_2\cdot COCl)_2$.

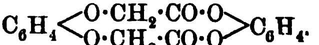
Resorcinolmono-oxyacetic acid, $OH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$, is formed, together with the dioxy-acid, by the action of ethyl monochloroacetate on a mixture of sodium ethoxide and resorcinol in ethyl alcoholic solution. Its *ethyl* ester separates from benzene in monoclinic pyramids, m. p. 55°. Various data quoted by Carter and Lawrence (Trans., 1900, 77, 1222) are confirmed. *Resorcinoldioxyacetyl chloride*, $C_6H_4(O\cdot CH_2\cdot COCl)_2$, is an oil, b. p. 232°/12—60 mm. (decomp.).

[With F. Ulmann.]—*Bisbromopropionylresorcinol*, $C_6H_4(O\cdot CO\cdot CHBrMe)_2$, obtained by the action of bromopropionyl bromide on disodium resorcinol in benzene solution, separates from alcohol in colourless crystals, m. p. 66°, and b. p. 217—220°/10 mm. As products of its interaction with disodium resorcinol, tribromoresorcinol and resorcinol bis-*a*-oxypropionic acid were obtained. The interaction with disodium catechol and disodium quinol gave tarry products.

Bis-a-bromobutyrylresorcinol, $C_6H_4(O\cdot CO\cdot CHEtBr)_2$, is a bright yellow oil, b. p. 225—227°/19 mm. *Bis-a-bromo*iso*butyrylresorcinol* has m. p. 61° and b. p. 227—228°/20 mm.

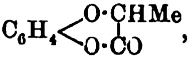
*Bis-a-bromo*iso*valerylresorcinol*, $C_6H_4(O\cdot CO\cdot CHBr\cdot CHMe_2)_2$, is a viscid, yellow oil, b. p. 222—228°/15 mm.

[With Differt.]—*Quinoldioxyacetyl chloride*, $C_6H_4(O\cdot CH_2\cdot COCl)_2$, obtained from the corresponding acid previously prepared by Carter and Lawrence (*loc. cit.*), forms colourless crystals, m. p. 84°, and has b. p. 240°/12—100 mm. (decomp.). It interacts with disodium quinol to form quinolbisoxyacetylquinol,



$$C_6H_4{<}\begin{matrix}O\cdot CH_2\cdot CO\cdot O\\ O\cdot CH_2\cdot CO\cdot O\end{matrix}{>}C_6H_4.$$

Bis-a-bromopropionylquinol, $C_6H_4(O\cdot CO\cdot CHMeBr)_2$, obtained from *a*-bromopropionyl bromide and disodium quinol, separates from benzene in colourless prisms, m. p. 110°. It interacts with disodium catechol to form *catecholoxypropiolactone*,



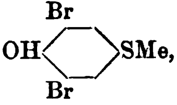
$$C_6H_4{<}\begin{matrix}O\cdot CHMe\\ |\\ O\cdot CO\end{matrix}$$

, m. p. 51°.

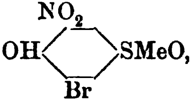
Bis-a-bromobutyrylquinol, $C_6H_4(O\cdot CO\cdot CHEtBr)_2$, forms colourless leaflets, m. p. 67—68°. *Bis-a-bromo*iso*butyrylquinol* forms colourless needles, m. p. 120°. *Bis-a-bromo*iso*valerylquinol* separates from alcohol in colourless leaflets, m. p. 53°.

A. McK.

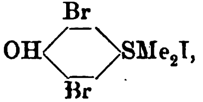
Preparation of Quinonoid Sulphur Compounds. Theodor Zincke and W. Glahn (*Ber.*, 1907, 40, 3039—3049).—The similarity between oxygen and sulphur suggested the possibility of preparing thioquinones of the type $O{:}C_6H_4{:}S$, and this investigation deals with the results obtained in the attempt. 2 : 6-*Dibromophenol*-4-*sulphonyl chloride*, $C_6H_8O_8ClBr_2S$, which crystallises in colourless needles, m. p. 127—128°, is easily prepared, the bromine shielding the hydroxyl group from the attack of the phosphorus pentachloride. On reduction with zinc and hydrochloric acid in alcoholic solution, 2 : 6-*dibromothioquinol*, $SH\cdot C_6H_4Br_2\cdot OH$, is obtained, crystallising in glistening needles, m. p. 82°. All attempts to convert this into the corresponding thiobenzoquinone have been fruitless; nitric acid oxidises it to picric acid, and ferric chloride gives 2 : 2′ : 6 : 6′-*tetrabromo*-4 : 4′-*diphenol disulphide*, $C_{12}H_6O_2Br_4S_2$, which crystallises in pale yellow needles, m. p. 152—153°. 2 : 6-*Dibromothioquinol diacetate* has m. p. 137—138°. With methyl iodide, the thioquinol yields, according to the conditions employed, a sulphide or a sulphonium iodide. When 1 mol. of the thioquinol dissolved in a solution of sodium methoxide (1 mol.) in methyl alcohol is treated with 1 mol. of methyl iodide in the cold, 2 : 6-*dibromophenol* 4-*methyl sulphide*,



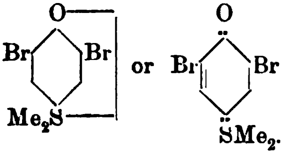
is formed, and crystallises in needles, m. p. 47—48°. Nitric acid oxidises the compound to picric acid. The *acetate*, $C_9H_8O_2Br_2S$, has m. p. 99°. When a dilute solution of sodium nitrite is carefully added to a cold solution of the dibromomethylthiolphenol in glacial acetic acid, 2-*bromo*-6-*nitrophenol* 4-*methyl sulphide*, $C_7H_6O_3NBrS$, is formed. It crystallises in red needles, m. p. 108°; the *acetate*, $C_9H_8O_4NBrS$, crystallises in dark yellow needles, m. p. 109—110°. Nitric acid in glacial acetic acid converts this sulphide into 2-*bromo*-6-*nitrophenol*-1-*methylsulphoxide*,



crystallising in yellow needles, m. p. 147—148°; the *acetate*, yellow needles, m. p. 106—107°. When 2 mols. of sodium methoxide and 2 of methyl iodide interact with the thioquinol at the b. p., 2 : 6-*dibromophenol*-4-*dimethylsulphonium iodide*,



separates on cooling. It crystallises from water in silky needles which lose methyl iodide at about 100°. The corresponding *sulphonium chloride*, $C_8H_9OClBr_2S$, obtained by the interaction of silver chloride and iodide in aqueous solution, crystallises in white, silky needles, losing methyl chloride at 160°. By shaking silver oxide with an aqueous solution of the sulphonium iodide, an anhydro-compound, 2 : 6-*dibromo*-1 : 4-*dimethylthioniumquinone*, is obtained. It may also be obtained by using alkali hydroxides. From water it crystallises in white plates, m. p. 251—252° (decomp.). Water regenerates the sulphide. 2 : 6-*Dinitro*-1 : 4-*dimethylthioniumquinone*, $C_8H_8O_5N_2S$, obtained by heating the sulphonium iodide with nitric acid (D 1·4), crystallises in glistening, yellow leaflets, m. p. 263—264° (decomp.). Hydroxylamine and phenylhydrazine are without action on the compound. The *hydrochloride* and *sulphate* are colourless, and it forms a *platinichloride*, $(C_8H_9O_5N_2S)_2PtCl_6$. If, however, the nitration be carried out in glacial acetic acid solution with less acid, 2-*bromo*-6-*nitro*-1 : 4-*dimethylthioniumquinone*,



$C_8H_8O_3NBrS$,

is the product. It is more stable than the dinitro-compound, crystallises in yellow needles, m. p. 270—271° (decomp.), and forms more stable salts and a *platinichloride*, $(C_8H_9O_3NBrS)_2PtCl_6$.

2 : 6-*Dinitrophenol* 4-*methyl sulphide*, $C_7H_6O_5N_2S$, prepared by digesting the dinitrodimethylthioniumquinone with 25% hydrobromic acid, forms dark red needles, m. p. 104—105°; the *acetate*, yellow needles, m. p. 129—130°. The corresponding *sulphoxide*, $C_7H_6O_6N_2S$, forms light yellow leaflets, m. p. 150°; the *acetate*, yellow needles, m. p. 137° (decomp.).

The conclusion is drawn that the more probable formula for the thionium compounds is the quinonoid. W. R.

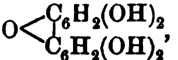
The Ethereal Function in Dichloromethylenecatechol.

Raymond Delange (*Compt. rend.*, 1907, **144**, 1278—1280).—The conversion of compounds containing the group $:O_2:CCl_2$ into the corresponding carbonates containing the group $:O_2:CO$ by the action of cold water (Abstr., 1904, i, 313, 741) is found to be a general reaction. Thus *ethyl dichloropiperonylate*, $CCl_2:O_2:C_6H_3\cdot CO_2Et$, having b. p. 156—157°/9 mm., gives the *carbonate*, $CO:O_2:C_6H_3\cdot CO_2Et$, which has b. p. 169—171°/12 mm., whilst *dichloropiperonyl chloride*, $CCl_2:O_2:C_6H_3\cdot COCl$, having b. p. 149—151°/13 mm., gives a mixture of the *carbonate*, $CO:O_2:C_6H_3\cdot CO_2H$, and 3 : 4-dihydroxybenzoic acid.

Fittig and Remsen (*Annalen*, 1869, **149**, 157) by the action of water on tetrachloropiperonal, $CCl_2:O_2:C_6H_3\cdot CHCl_2$, obtained a substance which they considered to be dichloropiperonal, $CCl_2:O_2:C_6H_3\cdot CHO$. The author having obtained tetrachloropiperonal as crystals, m. p. 34°, b. p. 162—164°/14 mm., has prepared Fittig and Remsen's compound, which, however, he considers to be, not dichloropiperonal, but *dichloromethylcatechol carbonate*, $CO:O_2:C_6H_3\cdot CHCl_2$, since (1) the group $:O_2:CCl_2$ is more readily attacked by water than is the group $\cdot CHCl_2$; (2) when boiled with water or dilute acids it gives 3 : 4-dihydroxybenzaldehyde; (3) it does not combine with sodium hydrogen sulphite, and (4) when treated with phosphorus pentachloride it does not regenerate tetrachloropiperonal, but remains unchanged.

Potassium hydroxide acts very violently on the dichloromethylenic ethers, forming compounds containing the group $:O_2:C:C:O_2:$; thus propyl catechol dichloromethylene ether gives the *compound* $C_6H_3Pr^{\alpha}:O_2:C:C:O_2:C_6H_3Pr^{\alpha}$, b. p. 242—243°/10 mm., which by dissolving in sulphuric acid and pouring the solution into water gives propylcatechol carbonate and *propylcatecholmethylenedisulphonic acid*, $C_6H_3Pr^{\alpha}:O_2:C(SO_3H)_2$, m. p. 52°. E. H.

Diphenyl Derivatives of Hydroxyquinol Trimethyl Ether [1 : 2 : 4-Trimethoxybenzene]. Action of Nitric Acid on Hydroxyquinol Trimethyl Ether.

Adolf Schüler (*Arch. Pharm.*, 1907, **245**, 262—283).—When the triacetate of hydroxyquinol, prepared from quinone by Thiele's method (Abstr., 1900, i, 505), is added to methyl or ethyl alcoholic sodium methoxide or ethoxide, and the resulting sodium derivative is methylated by the addition of methyl sulphate gradually and with constant shaking, then, if the 1 : 2 : 4-trimethoxybenzene formed is separated by distillation with steam instead of by shaking with ether, a by-product crystallises from the residue after distillation. This substance appears to be a 2 : 4 : 5 : 2′ : 4′ : 5′-*hexahydroxydiphenyl*, $C_6H_2(OMe)_3{\cdot}C_6H_2(OMe)_3$ (molecular weight determined cryoscopically in naphthalene); m. p. 177°. The fact that it does not yield a nitro-derivative makes it probable that no para-hydrogen atom is present; boiling with concentrated hydriodic acid converts it into 4 : 5 : 4′ : 5′-*tetrahydroxydiphenylene*-2 : 2′-*oxide*,  $O{<}\begin{matrix}C_6H_2(OH)_2\\ C_6H_2(OH)_2\end{matrix}$, m. p. 252°, which decomposes without melting when it is heated and forms an *acetyl* derivative.

1 : 2 : 4-Trimethoxybenzene forms a mononitro-derivative when nitrated in acetic acid solution in the cold; as the corresponding amino-derivative is oxidised readily to a quinone, probably the nitro-group is in the para-position to one of the methoxyl groups. 5-*Nitro*-1 : 2 : 4-*trimethoxybenzene*, $NO_2{\cdot}C_6H_2(OMe)_3$, m. p. 129°, is yellow. It is reduced by tin and hydrochloric acid to 5-*amino*-1 : 2 : 4-*trimethoxybenzene*, $NH_2{\cdot}C_6H_2(OMe)_3$, m. p. 94·5—95°; *hydrochloride*, m. p. 210° (decomp.); *benzoyl* derivative, m. p. 139·5—140°; this base is unstable in the air; 50% nitric acid, and nitrous acid also, oxidise it to 2 : 5-*dimethoxy*-p-*benzoquinone*, $C_6H_2O_2(OMe)_2$, which is yellow, decomposes without melting when it is heated, and is reduced by sulphurous acid to 2 : 5-dihydroxy-1 : 4-dimethoxybenzene, $C_6H_2(OH)_2(OMe)_2$, m. p. 170° (not 166°, Nietzki and Rechberg, Abstr., 1890, 968).

A dinitro-derivative of 1 : 2 : 4-trimethoxybenzene could not be obtained; the substance, m. p. 131°, described under this name (Will, Abstr., 1888, 457) was the mononitro-derivative just described. When a solution of the ether is added to dilute nitric acid and a reaction is induced by heating cautiously, oxidation takes place to a yellow substance, which decomposes without melting when it is heated, and appears to be a diphenylquinone with some such constitution as $OMe{\cdot}C_6H_2O_2{\cdot}C_6H_2O_2{\cdot}OMe$. C. F. B.

Transformation of Anethole Glycol into Anisylacetone. MARC TIFFENEAU and DAUFRESNE (*Compt. rend.*, 1907, **144**, 1354—1356. Compare Abstr., 1902, i, 666; 1904, i, 63, 133; 1906, i, 662, 724, 965; 1907, i, 130).—In previous papers the tranformation of α-glycols into aldehydes or ketones has been dealt with, and in view of Balbiano and Paolini's statement that α-glycols of the type OH·CHAr·CHR·OH, where Ar is an aryl radical, are converted by treatment with zinc chloride into hydrocinnamaldehydes, it has been thought desirable to ascertain whether the reaction represented by the scheme

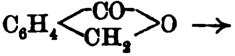
$$OH{\cdot}CHAr{\cdot}CHR{\cdot}OH \longrightarrow CHAr{:}CR{\cdot}OH \longrightarrow CH_2Ar{\cdot}COR,$$

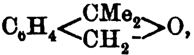
previously suggested (Tiffeneau, Abstr., 1907, i, 404), is of general application.

The diacetyl derivative of anethole glycol, obtained by heating anethole dibromide, dissolved in acetic acid, with lead or silver acetate (Balbiano and Paolini, Abstr., 1902, i, 808), has D⁰ 1·127, b. p. 187—189°/12 mm. The α-acetoxy-β-bromo-derivative, simultaneously produced (Hoering, Abstr., 1905, i, 903), has D⁰ 1·46, and b. p. 180—185°/14 mm., and on distillation is partially decomposed, yielding the *bromo*-derivative, $OMe\cdot C_6H_4\cdot CH{:}CMeBr$. This has D^0 1·325 and distils at 153—154° under 15 mm. pressure. When anethole dibromide dissolved in acetic acid is heated with zinc acetate, *p*-methoxyhydratropaldehyde is produced.

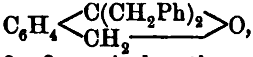
Anethole glycol, $OMe\cdot C_6H_4\cdot C_3H_5(OH)_2$ (Balbiano and Nardacci, Abstr., 1902, i, 808), on distillation under reduced pressure, furnishes a crystalline *substance*, m. p. 98°, b. p. 240—250°/14 mm., which may be the corresponding diethylenic oxide, and when treated with sulphuric acid is converted into anisylacetone. T. A. H.

Action of Organo-magnesium Compounds on Phthalide.

ALEXANDER LUDWIG (*Ber.*, 1907, 40, 3060—3065).—The behaviour of organo-magnesium compounds with alkylated phthalimides (Sachs and Ludwig, Abstr., 1904, i, 266; Béis, *ibid.*, i, 503) and "saccharins" (Sachs and Ludwig, *ibid.*, i, 876) led the author to examine the reaction between the Grignard reagent and phthalide. With an excess (3 mols.) of the reagent it proceeds thus:  $C_6H_4\left<\begin{matrix}CO\\CH_2\end{matrix}\right>O \rightarrow$ $C_6H_4\left<\begin{matrix}CR_2\cdot OH\\CH_2\cdot OH\end{matrix}\right.$, and this primary-tertiary alcohol yields by solution in sulphuric acid an intensely coloured liquid from which water precipitates colourless *as*-dialkyl-*o*-xylylene oxides, $C_6H_4\left<\begin{matrix}CR_2\\CH_2\end{matrix}\right>O$, which the author proposes to call dialkylphthalans.

The following compounds are described: *o-methylolphenyldimethylcarbinol*, $OH\cdot CH_2\cdot C_6H_4\cdot CMe_2\cdot OH$, m. p. 63—64°; 1 : 1-*dimethyl*-1 : 2-*dihydroisobenzofuran* (as-*dimethyl*-o-*xylylene oxide*, *dimethylphthalan*),  $C_6H_4\left<\begin{matrix}CMe_2\\CH_2\end{matrix}\right>O$, is an oil with a terpene-like odour; o-*methylolphenyldiethylcarbinol*, $OH\cdot CH_2\cdot C_6H_4\cdot CEt_2\cdot OH$, m. p. 81—82°; o-*methylolphenyldiisopropylcarbinol*, $OH\cdot CH_2\cdot C_6H_4\cdot CPr^{\beta}_2\cdot OH$, m. p. 107—108°; o-*methylolphenyldibenzylcarbinol*,

$$OH\cdot CH_2\cdot C_6H_4\cdot C(CH_2Ph)_2\cdot OH,$$

m. p. 133—134·5°, and its *acetyl* derivative, m. p. 103—104°. The preceding carbinol is insoluble in concentrated sulphuric acid, but when the solution in glacial acetic acid is boiled with concentrated hydrochloric acid and diluted with water, *dibenzylphthalan*,  $C_6H_4\left<\begin{matrix}C(CH_2Ph)_2\\CH_2\end{matrix}\right>O$, m. p. 88—89°, is obtained, which forms crystals 2—3 cm. in length. C. S.

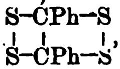
Thiobenzoic Acids.

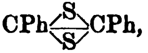
EMIL FROMM and PH. SCHMOLDT (*Ber.*, 1907, 40, 2861—2870).—Both benzoyl disulphide and thiobenzoyl disulphide contain the grouping $-\ddot{C}\cdot S\cdot S\cdot \ddot{C}-$, and are consequently found to follow Fromm's rule (Abstr., 1906, i, 656), being decomposed on heating or on treatment with alkalis, ammonia, and amines with the separation of sulphur.

Benzoyl disulphide is most readily prepared by the action of potassium ferricyanide on dilute solutions of thiobenzoates; it is decomposed by potassium hydroxide with the formation of thiobenzoic and benzoic acids and liberation of sulphur.

Thiobenzoyl disulphide cannot be prepared by acting on phenylcarbithionic acid (dithiobenzoic acid) with potassium ferricyanide, but is readily obtained by Houben and Pohl's method (Abstr., 1906, i, 847). It is decomposed by alcoholic potassium hydroxide into phenylcarbithionic and benzoic acids with liberation of sulphur, and by aniline with the formation of thiobenzanilide and the separation of sulphur.

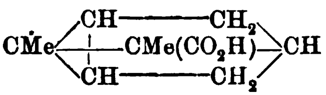
When either thiobenzoic acid, benzoyl sulphide, or benzoyl disulphide are distilled, they decompose yielding the same decomposition products, namely, hydrogen sulphide, sulphur, benzoic acid, and tolane tetrasulphide, a compound isomeric with thiobenzoyl disulphide (Houben and Pohl, *loc. cit.*).

Tolane tetrasulphide,  $\begin{array}{c}\mathrm{S{-}CPh{-}S}\\ |\quad\;|\quad\;|\\ \mathrm{S{-}CPh{-}S}\end{array}$, forms colourless crystals, m. p. 164°; it is not decomposed by ammonia or aniline, but is converted by alcoholic potassium hydroxide into 2 : 3 : 4 : 5-tetraphenylthiophen. This latter compound is also obtained from tolane tetrasulphide on reduction and by distillation over copper powder.

When lead phenylcarbithionate (dithiobenzoate) is submitted to dry distillation, it decomposes into lead sulphide, sulphur, and *tolane disulphide*,  $\mathrm{CPh}\langle{}^{\mathrm{S}}_{\mathrm{S}}\rangle\mathrm{CPh}$, which crystallises in needles, m. p. 174—175°, and is similar to tolane tetrasulphide in properties, being stable towards aniline and converted by potassium hydroxide, by distillation with copper powder, or by reduction, into 2 : 3 : 4 : 5-tetraphenylthiophen.

Benzylidene chloride is converted by sodium sulphide into β-trithiobenzaldehyde, and by sodium hydrosulphide into benzyl disulphide; phenylcarbithionic acid is not formed in the latter case as stated by Klinger (Abstr., 1882, 1058). W. H. G.

Constituents of Ethereal Oils—Teresantalic Acid, its Derivatives, and Constitution. FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 3101—3107. Compare Guerbet, Abstr., 1900, i, 242; Müller, *ibid.*, i, 678).—The optical properties of teresantalic acid derivatives indicate that these compounds belong to a saturated tricyclic series of quite different constitution, however, from the tricyclic santalol and eksantalol series (this vol., i, 431). The annexed formula is suggested for teresantalic acid.



Teresantalic acid has $[\alpha]_D^{18}$ 70°24′. The *methyl* ester, $C_{11}H_{16}O_2$, obtained by leaving the silver salt with an excess of methyl alcohol in a spacious separating funnel for some time, has b. p. 85—86°/11 mm.; D^{20} 1·032, and n_D 1·47053. When reduced with sodium and alcohol, the ester yields *teresantalol*, $C_{10}H_{16}O$, which may be crystallised from light petroleum; m. p. 113°, b. p. 95—98°/9 mm., $[\alpha]_D$ +11°58′. It sublimes with the greatest readiness. The *acetate* has b. p. 102—103°/9—10 mm., D^{20} 1·019, n_D 1·470. *Teresantalyl chloride*, $C_{10}H_{15}Cl$, obtained by the action of phosphorus pentachloride on an ethereal solution of the alcohol, has b. p. 78—85°/9 mm. and D^{20} 1·0656. *Teresantalan*, $C_{10}H_{16}$, has b. p. 165—168°, D^{20} 0·892, and n_D 1·48033. The hydrochloride of teresantalic acid has m. p. 199°, and when reduced yields *dihydroteresantalic acid*, $C_{10}H_{16}O_2$, m. p. 226°. The corresponding *methyl* ester, $C_{11}H_{18}O_2$, has b. p. 88°/9 mm., D^{20} 1·0034, n_D 1·46757, and is lævorotatory.

Dihydroteresantalol, $C_{10}H_{18}O$, obtained by reducing either the above methyl ester or, better, teresantalol, has b. p. 171°; *dihydroteresantalyl chloride*, $C_{10}H_{17}Cl$, has b. p. 70—75°/9 mm., and *dihydroteresantalan*, $C_{10}H_{18}$, b. p. 48—58°/9 mm. These reduction products have a saturated dicyclic constitution. J. J. S.

Ethyl Hexahydrobenzoylacetate. NICOLAI D. ZELINSKY and D. SCHWEDOFF (*Ber.*, 1907, **40**, 3055—3056).—*Ethyl hexahydrobenzoylacetate*, $C_6H_{11}\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 135—137°/18 mm., D^{18} 0·9678, is obtained by the action of equal molecular quantities of ethyl acetate and hexahydrobenzoate on finely-divided sodium. Ferric chloride produces an intense violet-red coloration. C. S.

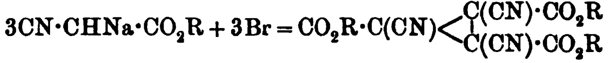
1 : 4-Diaminohexahydroterephthalic Acid. NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1907, **40**, 2888—2890. Compare this vol., i, 720).—1 : 4-*Diaminohexahydroterephthalonitrile*, $C_6H_8(CN)_2(NH_2)_2$, is formed when diketohexamethylene (*cyclo*hexane-1 : 4-dione) is condensed with potassium cyanide and ammonium chloride in concentrated aqueous solution in the cold. It separates in the form of colourless crystals which decompose at 193° without melting. It is extremely unstable and is decomposed even by cold water. It is hydrolysed to the corresponding acid when added to ice-cold concentrated sulphuric acid, kept for two days, and then warmed on the water bath. When cold, the *sulphate*, $C_6H_8(CO_2H)_2(NH_2)_2,H_2SO_4$, crystallises out. It does not melt at 285° and is hydrolysed by water. The *acid*, $C_8H_{14}O_4N_2$, forms a crystalline powder insoluble in the ordinary solvents, but dissolves in both alkalis and dilute mineral acids. It does not melt at 295°. A platinichloride could not be obtained. A small amount of a second amino-acid was obtained from the mother liquor from which the diaminohexahydroterephthalic acid had separated. J. J. S.

1 : 4-Dihydroxyhexahydroterephthalic Acid. NICOLAI ZELINSKY and N. SCHLESINGER (*Ber.*, 1907, **40**, 2890—2891).—1 : 4-*Dihydroxyhexahydroterephthalonitrile*, $C_6H_8(OH)_2(CN)_2$, has been synthesised from *cyclo*hexane-1 : 4-dione (diketohexamethylene) and hydrogen cyanide. It is sparingly soluble in water, alcohol, or ether, m. p. 152—154° (decomp.). When hydrolysed by adding it gradually to concentrated sulphuric acid, diluting with two volumes of water, and boiling for an hour, it yields the corresponding *acid*, $C_6H_8(OH)_2(CO_2H)_2$, which crystallises from hot water in colourless needles, m. p. 122°, with partial sublimation and decomposition. It is only sparingly soluble in cold water or cold alcohol. The *barium* salt crystallises in prisms containing $3H_2O$. J. J. S.

***cyclo*Trimethylene Compounds. III. Synthesis of *cyclo*-Propanecarboxylic Acids.** ARTHUR KÖTZ [and, in part, G. KAYSER, A. KEMPE, J. SIELISCH] (*J. pr. Chem.*, 1907, [ii], 75, 433—516. Compare Kötz and Stalmann, Abstr., 1903, i, 741; Kötz, *ibid.*, 742).—The first half of this paper consists of an account of the properties and the methods of synthesis of the *cyclo*propanecarboxylic acids. It is shown that the stability of the *cyclo*propane nucleus depends on the nature and position of the substituting groups, resolution of the ring taking place only between two carbon atoms, to one of which is attached a carboxyl group, whilst the other carries at least one substituting group other than carboxyl. The resolution takes place the more easily the fewer the hydrogen atoms attached to the two carbons concerned. The ring cannot be resolved in the absence of carboxyls, or between two carbon atoms each carrying a carboxyl, or if the compound contains a CH_2 and two $C\cdot CO_2H$ groups.

The methods of synthesis of the *cyclo*propanecarboxylic acids fall under three heads:

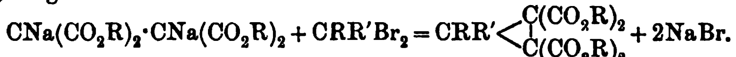
I. Synthesis from three molecules, each supplying one ring carbon atom:



$$3CN\cdot CHNa\cdot CO_2R + 3Br = CO_2R\cdot C(CN){<}\begin{array}{l}C(CN)\cdot CO_2R\\ C(CN)\cdot CO_2R\end{array} + 3NaBr.$$

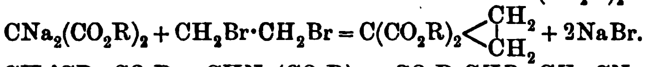
II. Syntheses from two molecules, one supplying one, the other, two, ring carbon atoms:

1.



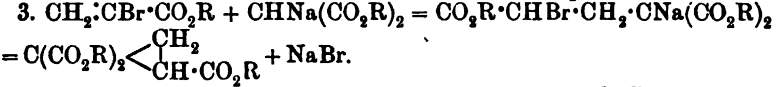
$$CNa(CO_2R)_2\cdot CNa(CO_2R)_2 + CRR'Br_2 = CRR'{<}\begin{array}{l}C(CO_2R)_2\\ C(CO_2R)_2\end{array} + 2NaBr.$$

2.



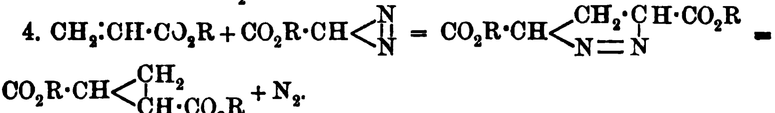
$$CNa_2(CO_2R)_2 + CH_2Br\cdot CH_2Br = C(CO_2R)_2{<}\begin{array}{l}CH_2\\ CH_2\end{array} + 2NaBr.$$

3.



$$CH_2{:}CBr\cdot CO_2R + CHNa(CO_2R)_2 = CO_2R\cdot CHBr\cdot CH_2\cdot CNa(CO_2R)_2 = C(CO_2R)_2{<}\begin{array}{l}CH_2\\ CH\cdot CO_2R\end{array} + NaBr.$$

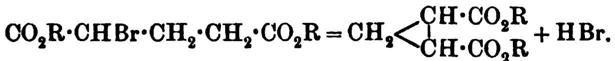
4.



$$CH_2{:}CH\cdot CO_2R + CO_2R\cdot CH{<}\begin{array}{l}N\\ N\end{array} = CO_2R\cdot CH{<}\begin{array}{l}CH_2\cdot CH\cdot CO_2R\\ N{=}N\end{array} = CO_2R\cdot CH{<}\begin{array}{l}CH_2\\ CH\cdot CO_2R\end{array} + N_2.$$

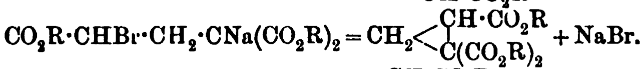
III. Syntheses in which the three-ring carbon atoms are derived from one molecule:

1.



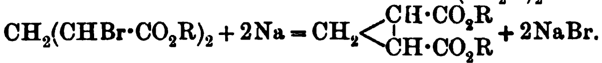
$$CO_2R\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO_2R = CH_2{<}\begin{array}{l}CH\cdot CO_2R\\ CH\cdot CO_2R\end{array} + HBr.$$

2.



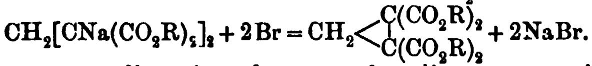
$$CO_2R\cdot CHBr\cdot CH_2\cdot CNa(CO_2R)_2 = CH_2{<}\begin{array}{l}CH\cdot CO_2R\\ C(CO_2R)_2\end{array} + NaBr.$$

3.



$$CH_2(CHBr\cdot CO_2R)_2 + 2Na = CH_2{<}\begin{array}{l}CH\cdot CO_2R\\ CH\cdot CO_2R\end{array} + 2NaBr.$$

4.



$$CH_2[CNa(CO_2R)_2]_2 + 2Br = CH_2{<}\begin{array}{l}C(CO_2R)_2\\ C(CO_2R)_2\end{array} + 2NaBr.$$

The propane-di-, -tri-, and -tetra-carboxylic esters required for the syntheses under III. are prepared by the general reactions:

1. Polymerisation of esters of the acrylic series:

$$2CH_2{:}CH\cdot CO_2R = CH_2{:}C(CO_2R)\cdot CH_2\cdot CH_2\cdot CO_2R,$$

and hydrolysis of the resulting alkylideneglutaric ester with formation of a propane-$\alpha\gamma$-dicarboxylic acid and an aldehyde or a ketone.

2. Addition of ethyl malonate to esters of the acrylic series: $CH_2{:}CH\cdot CO_2R + CH_2(CO_2R)_2 = CH(CO_2R)_2\cdot CH_2\cdot CH_2\cdot CO_2R$.

3*a*. Addition of ethyl malonate to esters of the methylenemalonic series: $CH_2{:}C(CO_2R)_2 + CH_2(CO_2R)_2 = CH_2[CH(CO_2R)_2]_2$.

3*b*. Action of dihaloids derived from aldehydes or ketones on ethyl sodiomalonate: $CRR'Br_2 + 2CHNa(CO_2R)_2 = CRR'[CH(CO_2R)_2]_2 + 2NaBr$.

The esters of the acrylic series are formed by condensation of aldehydes and ketones with acetic acid, and those of the methylenemalonic series by condensation of aldehydes and ketones with ethyl malonate, or by the action of dihaloids derived from aldehydes or ketones, on ethyl disodiomalonate.

The following new experimental details are given in the second half of the paper.

Ethyl α-bromopropane-ααγγ-tetracarboxylate, formed by bromination of ethyl propane-$\alpha\alpha\gamma\gamma$-tetracarboxylate cooled by ice, decomposes when distilled, and when treated with methyl alcoholic ammonia at the ordinary temperature yields ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate.

Ethyl propylidenemalonate, $CHEt{:}C(CO_2Et)_2$, is obtained by heating ethyl malonate with propaldehyde and acetic anhydride under pressure at 100°, in a 90% yield, as a transparent liquid, b. p. 115—125°/12 mm., and on prolonged shaking with concentrated ammonia is partly hydrolysed and partly decomposed forming propaldehyde and malonamide.

Ethyl propylidenedimalonate, $CHEt[CH(CO_2Et)_2]_2$, formed by the action of ethyl sodiomalonate on ethyl propylidenemalonate in ethereal solution, is obtained as a slightly yellow liquid, b. p. 195—205°/12 mm. When converted into its *disodio*-derivative and treated with iodine in ethereal solution, it yields ethyl ethylenetetracarboxylate, ethyl ethanetetracarboxylate, and *ethyl 3-ethyl*cyclo*propane*-1 : 1 : 2 : 2-*tetracarboxylate*, b. p. 211—240°/12 mm., which on hydrolysis with aqueous ammonia forms the *acid* as a reddish-brown, viscid mass with an odour resembling that of the fatty acids. The *silver* salt, $C_9H_6O_8Ag_4$, was analysed. 3-*Ethyl*cyclo*propane*-1 : 2-*dicarboxylic acid*, obtained by hydrolysis of the tetracarboxylic ester with alcoholic potassium hydroxide and evaporation of the product with hydrochloric acid in an atmosphere of carbon dioxide, forms a hygroscopic, white, crystalline mass; the *silver* salt, $C_7H_8O_4Ag_2$, was analysed; the *ethyl* ester, b. p. 185—195°/12 mm. (decomp.). On distillation, the dicarboxylic acid decomposes, yielding ethylparaconic acid and an oil which may be hydrosorbic acid.

Ethyl αβγ-triethylpropane-ααγγ-tetracarboxylate, b.p. 195—230°/12 mm. (decomp.), formed together with ethyl propylidenemalonate and ethyl ethylmalonate by the action of sodium and ethyl iodide on ethyl propylidenedimalonate in alcoholic solution, yields ethylmalonamide when treated with concentrated ammonia, and on hydrolysis with hydrochloric acid forms *αβγ-triethylglutaric acid*, obtained as a yellow, viscid mass, and analysed in the form of its *silver* salt, $C_{11}H_{18}O_4Ag_2$.

Tri-γ-chlorocrotonic acid, $CCl_3\cdot CH{:}CH\cdot CO_2H$, formed by hydrolysis of ethyl trichloroethylidenemalonate by means of boiling 27% hydrochloric acid, separates from water in stout crystals, m.p. 119°.

Ethyl trichloroethylidenedimalonate, $CCl_3\cdot CH[CH(CO_2Et)_2]_2$, prepared from ethyl trichloroethylidenemalonate and ethyl sodiomalonate, is obtained as a yellow oil which decomposes at 60°. On hydrolysis with hydrochloric acid, it yields *β-trichloromethylglutaric acid*,

$$CCl_3\cdot CH(CH_2\cdot CO_2H)_2,$$

which crystallises from benzene in nacreous leaflets, m. p. 159°.

*Ethyl 3-trichloromethyl*cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate*, m. p. 48°, is formed by the action of bromine on ethyl trichloroethylidenedimalonate or on its disodio-derivative.

Ethyl a-bromo-β-phenylpropane-aaγγ-tetracarboxylate,

$$CH(CO_2Et)_2\cdot CHPh\cdot CBr(CO_2Et)_2,$$

decomposes on distillation; when treated with methyl alcoholic ammonia, it yields ethyl 3-phenyl*cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate, b. p. 228°/11 mm., which on hydrolysis is converted into 3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid, m. p. 175°. The oil, b. p. 100—200°/12 mm., described by Kötz and Stalmann (*loc. cit.*), is shown to have been a mixture of benzaldehyde, ethyl malonate, and ethyl ethylenetetracarboxylate. In agreement with this, ethyl disodio-β-phenylpropane-*aaγγ*-tetracarboxylate is decomposed by dilute acids, forming ethyl malonate and ethyl benzylidenemalonate, together with only traces of ethyl 3-phenyl*cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate. Similarly, ethyl disodioethylidenedimalonate is decomposed by dilute acids, forming ethyl malonate and ethyl ethylidenemalonate. The action of methyl iodide on ethyl dipotassio-β-phenylpropane-*aaγγ*-tetracarboxylate leads to the formation of ethyl methylmalonate and ethyl benzylidenemalonate.

*Ethyl a-bromo*iso*propylmalonate*, formed by the action of bromine on ethyl *iso*propylmalonate cooled by ice, is obtained as a colourless liquid, b. p. 119—123°/12 mm. or 215—230°/760 mm. When heated with diethylaniline in a reflux apparatus at 170—175°, it yields ethyl dimethylacrylate, ethyl malonate, and only small amounts of ethyl *iso*propylenemalonate, b. p. 110—112°/12 mm.; when shaken with concentrated aqueous ammonia, this yields acetone and malonamide. Ethyl ββ-dimethylpropanetetracarboxylate (Lawrence, Proc., 1899, 62), b. p. 190—195°/12 mm., is formed in a 90—95% yield by heating ethyl *iso*propylenemalonate with ethyl sodiomalonate in ethereal solution at 60—70° under pressure; when treated with bromine alone it is converted only partially into the *a-bromo*-derivative, but on treatment with bromine in presence of iodine in sunlight, it yields ethyl ethanetetracarboxylate.

*Ethyl 3 : 3-dimethyl*cyclo*propanetetracarboxylate*, formed by the action of methyl alcoholic ammonia on ethyl *a*-bromo-ββ-dimethylpropanetetracarboxylate, is obtained as a slightly yellow oil, b. p. 188—190°/10 mm., and on hydrolysis with alcoholic potassium hydroxide and subsequent boiling with hydrochloric acid, yields a mixture of *cis-* and *trans*-caronic acids (Perkin and Thorpe, Trans., 1899, 75, 48).

The action of bromine on ethyl disodio-ββ-dimethylpropanetetracarboxylate cooled by ice leads to the formation of ethyl ethanetetracarboxylate, whilst the action of water on the disodio-ester leads to the formation of ethyl malonate and ethyl *iso*propylenemalonate, and that of ethyl iodide in boiling alcoholic solution to the formation of ethyl *iso*propylenemalonate and ethyl ethylmalonate.

Ethyl dimethylacrylate remains unchanged in ethereal solution in presence of sodium methoxide, free from alcohol, at the ordinary temperature (compare Pechmann, Abstr., 1901, i, 63; Pechmann and Röhm, *ibid.*, 253).

Ammonia reacts with ethyl methylenemalonate with development of heat and formation of hexamethylenetetra-amine.

Ethyl m-*nitrobenzylidenemalonate,* prepared by condensation of *m*-nitrobenzaldehyde with ethyl malonate in presence of piperidine at 80°, crystallises in rhombic plates, m. p. 73°, decolorises potassium permanganate in ethereal solution, and reacts with ethyl sodiomalonate with development of heat, forming *ethyl sodio*-m-*nitrobenzylidenedimalonate.* On treatment with dilute sulphuric acid, this yields the free *ester* as a viscid, yellow oil, which decomposes on distillation/12 mm., and is hydrolysed by alcoholic potassium hydroxide to m-*nitrobenzylidenedimalonic acid*, or by hydrochloric acid to *β*-*m*-nitrophenylglutaric acid. This is formed also by the action of bromine on the disodiodimalonate or of sodium hydroxide on the viscid, yellow *bromodimalonate.* m-*Nitrobenzylidenedimalonic acid* forms a yellowish-red, amorphous mass, decomposing above 150°; the *silver* salt, $C_{18}H_7O_{10}NAg_4$, was analysed.

Ethyl *m*-nitrobenzylidenedimalonate is reduced by sodium and methyl alcohol to a yellowish-red, unstable *azoxy*-derivative, but by aluminium amalgam in alkaline solution to *ethyl* m-*aminobenzylidenedimalonate,* which is obtained as a yellowish-red, viscid oil, and on hydrolysis with hydrochloric acid yields *β*-m-*aminophenylglutaric acid hydrochloride.* This is formed also by reduction of *β*-*m*-nitrophenylglutaric acid with stannous chloride and hydrochloric acids; it forms white crystals, m. p. 100—101°, becomes red on exposure to air, gives an intensely-yellow lignin reaction, and when diazotised and boiled with sulphuric acid yields *β*-m-*hydroxyphenylglutaric acid*, m. p. 112°.

Ethyl p-*nitrobenzylidenedimalonate,* formed by condensation of the monomalonate with ethyl sodiomalonate, is converted by hydrolysis with hydrochloric acid into *p*-nitrophenylglutaric acid. When reduced with stannous chloride and hydrochloric acid, diazotised, and boiled with sulphuric acid, this yields *β*-p-*hydroxyphenylglutaric acid,* which forms white crystals, m. p. 154—155°.

β-m-2-*Naphtholazophenylglutaric acid*, formed by coupling diazotised *β*-*m*-aminophenylglutaric acid with *β*-naphthol in alkaline solution, is obtained as red, crystalline powder, m. p. 208°, is soluble in alkalis, and forms a red, insoluble *barium* salt. G. Y.

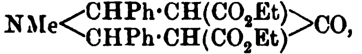
Condensation of Ethyl Acetonedicarboxylate with Aldehydes Under the Influence of Ammonia and Amines. II.

PAVEL PETRENKO-KRITSCHENKO and M. LEWIN [and, in part, F. MENTSCHIKOWSKY] (*Ber.*, 1907, 40, 2882—2885).—Cinnamaldehyde and furfuraldehyde react with acetonedicarboxylic esters in the presence of ammonia in quite a different manner from benzaldehyde

(Abstr., 1900, i, 307; 1906, i, 452), the products being 1 : 5-diketones (compare Knoevenagel, Abstr., 1896, i, 210). *Ethyl cinnamylidenebisacetonedicarboxylate*, $CHPh:CH\cdot CH[CH(CO_2Et)\cdot CO\cdot CH_2\cdot CO_2Et]_2$, is formed when a slow stream of dry ammonia is passed into a benzene solution of cinnamaldehyde and ethyl acetonedicarboxylate. The yield is increased when the ammonia is replaced by diethylamine. It separates from benzene in colourless crystals, m. p. 132—133°.

Furfuraldehyde and methyl acetonedicarboxylate in the presence of ammonia give a small yield of *methyl furfurylidenebisacetonedicarboxylate*, $C_4OH_3\cdot CH[CH(CO_2Me)\cdot CO\cdot CH_2\cdot CO_2Me]_2$, m. p. 162—175° (decomp.), which is sparingly soluble in hot alcohol. A by-product is an oily compound containing nitrogen. When diethylamine is used as the condensing agent, a product, m. p. 139—143°, is obtained. This is probably a mixture of the condensation product and the original ester.

Ethyl 2 : 6-*diphenyl*-1-*methylpiperidone*-3 : 5-*dicarboxylate*



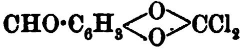
$$NMe<\begin{matrix}CHPh\cdot CH(CO_2Et)\\CHPh\cdot CH(CO_2Et)\end{matrix}>CO,$$

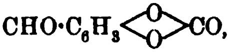
obtained by the condensation of acetonedicarboxylic ester and benzaldehyde in the presence of methylamine, or by the action of methyl iodide on the secondary base previously described (Abstr., 1906, i, 452), crystallises from alcohol in well developed prisms, m. p. 85—86°. The *hydrochloride*, $C_{24}H_{28}O_5NCl$, m. p. 195—200°, is insoluble in water or benzene and may be crystallised from a mixture of chloroform and light petroleum. With nitrous acid the ester yields a *nitrosoamine*, m. p. 137—139°. J. J. S.

Hexahydrobenzaldehyde. Nicolai D. Zelinsky and Johannes Gutt (*Ber.*, 1907, **40**, 3050—3053. Compare Bouveault, Abstr., 1904, i, 61; Wallach, 1906, i, 564).—Hexahydrobenzaldehyde, obtained from *cyclo*hexylcarbinol by oxidation with chromic acid, forms the *aldoxime*, $C_7H_{13}ON$, crystallising in needles, m. p. 90—91°; the *hydrochloride* has m. p. 107—108° (decomp). The solid polymeride of hexahydrobenzaldehyde (Wallach, *loc. cit.*) is $(C_7H_{12}O)_3$. When dimethylaniline and hexahydrobenzaldehyde condense, a green dye is formed, and on dissolution in alcohol the *leuco*-base (?), $C_{23}H_{32}N_2$, is deposited as white needles, m. p. 148—149°; this substance, however, cannot be re-oxidised to the dye.

The m. p. of hexahydrobenzylidenesemicarbazone is 173—174° (Wallach, 167—168°; Bouveault, 176°). W. R.

Diphenylhydrazones of the Tolualdehydes. F. Robive and Bernhard Tollens (*Ber.*, 1907, **40**, 3107. Compare Maurenbrecher, Abstr., 1906, i, 985). J. J. S.

Conversion of Piperonal into the Cyclic Carbonate of Protocatechualdehyde. Hermann Pauly (*Ber.*, 1907, **40**, 3096—3100).—A good yield of Fittig and Remsen's dichloropiperonal,  $CHO\cdot C_6H_3<\begin{matrix}O\\O\end{matrix}>CCl_2$ (*Annalen*, 1871, **159**, 126), can be obtained by acting with phosphorus pentachloride on piperonal and pouring the product on to ice, provided certain directions are followed. All acid must be completely removed by repeated washing with water. It crystallises from chloroform, has m. p. 96—97°, b. p. 178°/15 mm., and is stable when protected from moisture.

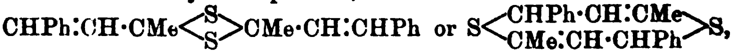
When heated with anhydrous oxalic acid at 130° and ultimately at 160°, it yields *protocatechualdehyde carbonate*,  $CHO\cdot C_6H_3<\begin{matrix}O\\O\end{matrix}>CO$, which may be distilled under reduced pressure. Treatment with cold concentrated sulphuric acid, or with anhydrous formic acid at 80—90°, yields the same product. It forms rhombic crystals, m. p. 124° (corr.), b. p. 162°(corr.)/13 mm., or 289° under atmospheric pressure. It reacts with alcohols yielding the monoalkyl carbonates. When boiled with water, it loses carbon dioxide quantitatively, and in the presence of small amounts of tertiary amines this decomposition proceeds in the cold. It is, however, relatively stable in the presence of concentrated acids. J. J. S.

Conversion of Substituted Adipic and Pimelic Acids into Cyclic Ketones. H. G. Blanc (*Compt. rend.*, 1907, **144**, 1356—1358).—When an acid of either of these groups is heated during some hours with acetic anhydride, it is converted into the corresponding anhydride, which, on slow distillation at the atmospheric pressure and at a temperature which varies for the different anhydrides, decomposes, yielding carbon dioxide and the corresponding cyclic ketone.

A number of these ketones have been prepared in this way, and of these the following are new: 1 : 1 : 4-*trimethyl*cyclo*pentane*-5-*one*, b. p. 152°, *oxime*, m. p. 62°; 1-*methyl*-3-*allyl*cyclo*pentane*-4-*one*, b. p. 188°, *semicarbazone*, m. p. 156°; 1 : 1 : 4-*trimethyl*cyclo*hexane*-5-*one*, b. p. 185°, *semicarbazone*, m. p. 170°. T. A. H.

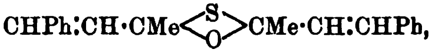
Action of Ammonia Sulphide on Ketones. Emil Fromm and H. Höller (*Ber.*, 1907, **40**, 2978—2982).—Manchot and Krische's supposed diphenyldimethylthiopinacone (Abstr., 1905, i, 142) is a mixture of 2 : 4-diphenylthiophen (Baumann and Fromm, Abstr., 1895, i, 363) and sulphur. G. Y.

Thio-derivatives of Ketones. V. Duplobenzylidenethioacetone, a Substance with Extraordinary Additive Powers. Emil Fromm and H. Höller (*Ber.*, 1907, 40, 2982—2993. Compare Fromm and Baumann, Abstr., 1889, 852; Baumann and Fromm, Abstr., 1890, 25; 1895, i, 362; Fromm and Ziersch, Abstr., 1906, i, 931).—The formation of thio-derivatives by the action of hydrogen sulphide on mono- and 1 : 3-di-ketones in presence of hydrogen chloride has been described in previous papers. The study of this reaction has been extended now to an unsaturated ketone, benzylideneacetone. This ketone is found to yield a product,



$$CHPh{:}CH\cdot CMe<\begin{matrix}S\\S\end{matrix}>CMe\cdot CH{:}CHPh \text{ or } S<\begin{matrix}CHPh\cdot CH{:}CMe\\CMe{:}CH\cdot CHPh\end{matrix}>S,$$

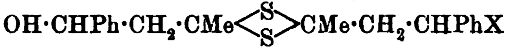
which the authors term *duplobenzylidenethioacetone*. The former formula is preferred, as it explains the more easily the transformation of the substance into *duplobenzylideneoxythioacetone*,



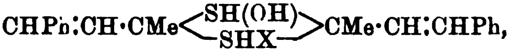
$$\mathrm{CHPh{:}CH{\cdot}CMe{<}_{O}^{S}{>}CMe{\cdot}CH{:}CHPh},$$

and the hydrolysis of this to benzylideneacetone.

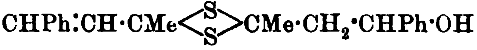
Duplobenzylidenethioacetone, $C_{20}H_{20}S_2$, separates from alcohol in crystals containing alcohol of crystallisation, which is lost readily on exposure to air, m. p. 132·5°, forms an unstable *additive* compound with bromine, and when boiled with acids in alcoholic solution yields *duplobenzylideneoxythioacetone*, $C_{20}H_{20}O_2,\frac{1}{2}H_2O$, m. p. 186·5°, soluble in ether. On evaporation, the mother liquor from the preparation of this yields benzylideneacetone. The action of dilute acids on duplobenzylidenethioacetone in warm alcoholic solution leads to the formation of the oxythioacetone together with the following *additive* products: $C_{20}H_{20}S_2,HCl,H_2O$, m. p. 229°; $C_{20}H_{20}S_2,HBr,H_2O$, m. p. 230°; $C_{20}H_{20}S_2{\cdot}H_2SO_4,H_2O$, m. p. 177°; $C_{20}H_{20}S_2,N_2O_3$, m. p. 197°. An *additive* product, $C_{20}H_{20}S_2,HCl$, m. p. 208°, is formed by the action of hydrogen chloride on duplobenzylidenethioacetone in ethereal solution and absorbs water readily. These *additive* compounds may have the constitution (I)



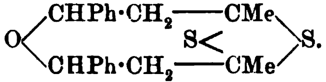
$\mathrm{OH{\cdot}CHPh{\cdot}CH_2{\cdot}CMe{<}_{S}^{S}{>}CMe{\cdot}CH_2{\cdot}CHPhX}$ or (II)



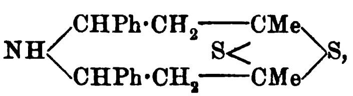
$\mathrm{CHPh{:}CH{\cdot}CMe{<}_{SHX}^{SH(OH)}{>}CMe{\cdot}CH{:}CHPh}$, are colourless, insoluble in ether, and when treated with boiling dilute alkalis or alkali carbonates yield *duplobenzylidenethioacetone hydrate*, $C_{20}H_{20}S_2,H_2O$ needles, m. p. 152°, or benzylideneacetone on prolonged boiling. The hydrate does not form a benzoyl derivative, but is readily converted into the acid *additive* compounds, which have therefore probably the formula (I). The hydrate may have the constitution



$\mathrm{CHPh{:}CH{\cdot}CMe{<}_{S}^{S}{>}CMe{\cdot}CH_2{\cdot}CHPh{\cdot}OH}$ or



The action of ammonia on the acid *additive* compounds leads to the formation of an *additive* compound, $C_{20}H_{20}S_2,NH_3$, which crystallises in needles, m. p. 142°, may have the annexed constitution, and is readily converted into the acid *additive* compounds by the action of cold dilute acids. An *additive* compound, $C_{20}H_{20}S_2,NH_3$, m. p. 148°, formed by the action of ammonia on duplobenzylidenethioacetone, may be identical or isomeric with the preceding derivative. G. Y.

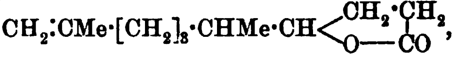


Condensations with Citronellal. II. HANS RUPE, S. PFEIFFER, and J. SPLITTGERBER (*Ber.*, 1907, **40**, 2813—2817. Compare Abstr., 1903, i, 841).—Citronellideneacetic acid,

$$\mathrm{CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H},$$

previously prepared from citronellal and malonic acid in the presence of pyridine, is a liquid with b. p. 175·5—177·5°/14 mm. Grünhagen (*Diss.*, 1898), using the same method, however, obtained the acid as a solid, m. p. 51—52°. The liquid, previously described, was a mixture of isomeric acids, one of which had the double linking in the $\beta\gamma$-position, since a lactone could be obtained by treatment with sulphuric acid. This transference of the double linking had taken place owing to the presence of the pyridine.

The *lactone*,



$CH_2{:}CMe\cdot[CH_2]_3\cdot CHMe\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CO\end{matrix}$, has b. p. 161—163°/13 mm.

βζ-Dimethyl-Δ^α^-nonene-αθ-ol,

$CH_2{:}CMe\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CHMe\cdot OH$,

obtained by the action of magnesium methyl iodide on citronellal, has b. p. 104—105°/10 mm., D_4^{20} 0·8578, $[\alpha]_D^{20}$ +0·55°. Its *acetate*, $C_{13}H_{24}O_2$, has b. p. 118—119°/14 mm.

βζ-Dimethylnonane-βθ-diol,

$OH\cdot CMe_2\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot CHMe\cdot OH$,

obtained by boiling the preceding alcohol with ethyl alcohol and sulphuric acid, has b. p. 144—145°/14 mm.

βζ-Dimethyl-Δ^{α}-nonene-θ-one, $CH_2{:}CMe\cdot[CH_2]_3\cdot CHMe\cdot CH_2\cdot COMe$, obtained by oxidising the dimethylnoneneol with potassium dichromate and sulphuric acid, has b. p. 93—94°/12 mm., D_4^{20} 0·8650, $[\alpha]_D^{20}$ +5·89°, n_D^{20} 1·4496. Its *semicarbazone* separates from dilute alcohol in glistening leaflets, m. p. 82—83°. Its *oxime* has b. p. 133—134°/11 mm. A. McK.

Bornyl and Fenchyl Derivatives. IWAN KONDAKOFF and IWAN SCHINDELMEISER (*J. pr. Chem.*, 1907, [ii], **75**, 529—538).—The action of phosphorus pentahaloids and of hydrogen haloids on secondary hydroaromatic alcohols is discussed. Previously the product of the reaction has been an unstable, or a mixture of this with a stable, haloid derivative (Abstr., 1895, i, 549). It is found possible now to increase the amount of either haloid derivative by varying the experimental conditions. The present work was undertaken to determine if the action of hydrogen haloids on the esters of the secondary hydroaromatic alcohols takes place in the same manner as the action of the hydrogen haloids on the alcohols, and, if possible, to obtain indications of an intermediate phase by means of which the complicated transformations of the alcohols might be explained.

Wagner and Brickner (Abstr., 1900, i, 46. Compare Hesse, Abstr., 1906, i, 375) showed that the action of phosphorus pentachloride on borneol leads to the formation of *iso*bornyl chloride or camphene hydrochloride, which is unstable, and a stable chloride which these authors assumed to be Kindt's camphor. It is found now that *l*-borneol acetate, which on hydrolysis yields *l*-borneol, on treatment with hydrogen chloride in acetic acid solution at 125°, yields pinene hydrochloride, m. p. 124°; this has the same m. p. when mixed with Kindt's camphor, is optically inactive, and is hydrolysed partially to camphor when heated with water at 120°. This is the first case of the conversion of the acetate into the corresponding *sec.*-chloride without simultaneous formation of a racemised stereoisomeride or a tertiary chloride.

Similar results are obtained with fenchyl acetate. Fenchyl alcohol sublimes in plates, m. p. 47°, $[\alpha]_D$ − 15°22′, and probably contains traces of fenchone. The acetate, b. p. 91—91·5°/12 mm., D^{20} 0·972,

$[\alpha]_D$ −63°24′, n_D 1·4565 (compare Bertram and Helle, Abstr., 1900, i, 398; Bouchardat and Lafont, Abstr., 1899, i, 156), is converted by hydrogen chloride in acetic acid solution at 125—130° into a chloride, b. p. 68—74°/11 mm., D^{20} 0·952, n_D 1·4758, which is optically inactive, reacts with silver nitrate, and on treatment with alcoholic potassium hydroxide yields considerable amounts of *i*-fenchene, but remains for the most part unchanged. The chloride, b. p. 76—78°/12 mm., obtained by the action of phosphorus pentachloride on fenchyl alcohol, does not react with silver nitrate. G. Y.

***iso*Fenchyl Alcohol and its Derivatives.** IWAN KONDAKOFF (*J. pr. Chem.*, 1907, [ii], 75, 539—548).—*iso*Fenchyl alcohol has been held by various authors to be (1) a mixture of structurally identical, but optically different, secondary alcohols (Bertram and Helle, Abstr., 1900, i, 398); (2) a mixture of tertiary alcohols or of a tertiary and a secondary alcohol; (3) a stereoisomeride of fenchyl alcohol (Abstr., 1900, i, 604), or (4) a mixture of two secondary alcohols of different types. As the experimental facts published previously do not admit of a decision between these views, the author gives now a number of observations made with *iso*fenchyl alcohol and its derivatives.

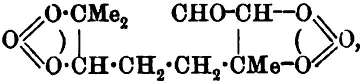
*iso*Fenchyl alcohol, prepared from fenchene by Bertram and Helle's (*loc. cit.*), Kondakoff's (*loc. cit.*, Abstr., 1902, i, 478), or Wallach's (Abstr., 1901, i, 331) method, is a mixture of a liquid and a crystalline alcohol; a portion of the fenchene remains always unchanged. A fenchene, b. p. 152—159°, $D^{17\cdot5}$ 0·860, $[\alpha]_D$ −36°3′, n_D 1·46643, formed an acetate, b. p. 100—105°/15 mm., D_4^{20} 0·9784, $[\alpha]_D$ +5°33′, n_D 1·46257; the alcohol, m. p. 61·5°, $[\alpha]_D$ +45°40′; the unchanged fenchene, b. p. 144—152°, D_4^{20} 0·8539, α_D −21°10′. Another fenchene, b. p. 155—158°, D_4^{20} 0·8677, $[\alpha]_D$ −39°50′, yielded a residual fenchene, b. p. 146—158°, D_4^{20} 0·8529, α_D −12°02′; the acetate was obtained in two fractions: b. p. 90—95·5°/15 mm., $[\alpha]_D$ −9°35′, and b. p. 95·5—100°/95 mm., $[\alpha]_D$ −7°38′. In both experiments an optically inactive acetate, b. p. 95—97°/15 mm., D_4^{20} 0·9752, n_D 1·46168, was obtained. On hydrolysis, the lævorotatory acetate gave an alcohol, $[\alpha]_D$ −6·07°, and the inactive acetate an alcohol, $[\alpha]_D^{17\cdot4}$ −6·31°. When mixed and distilled/10 mm., these alcohols gave a series of fractions: b. p. 80—81°, $D^{18\cdot5}$ 0·961, n_D 1·47751, optically inactive; b. p. 81—82°, $D^{20\cdot5}$ 0·952, $[\alpha]_D$ −2°, n_D 1·47654; b. p. 82—84·5°, $[\alpha]_D$ −5°; these three fractions did not solidify. A fourth fraction, b. p. 84·5—87°, yielded two crystalline alcohols: m. p. 48—53°, and m. p. 54—55°, $[\alpha]_D^{20\cdot5}$ −8·13° in ethyl alcoholic, or −7·06° in toluene, solution. Other preparations of crystalline *iso*fenchyl alcohols had $[\alpha]_D^{18}$ −8·75° and −11·6° respectively. It is evident that no relation can be established between the original and residual fenchenes, or between the acetates and the alcohols derived from them.

When treated with phosphorus pentachloride, an *i*-*iso*fenchyl alcohol, b. p. 80—81°, yielded a chloride which was obtained in two fractions: b. p. 73—74°/9 mm., D^{20} 0·996, $[\alpha]_D$ −3°53′, n_D 1·4812, and b. p. 74—76°/9 mm., $[\alpha]_D$ −5°2′. This chloride yielded silver chloride quantitatively with silver nitrate in alcoholic solution, gave with alcoholic potassium hydroxide an *iso*fenchyl alcohol, b. p. 71—74°/

8 mm., $D^{17.5}$ 0·932, n_D 1·46702, containing traces of chlorine together with small amounts of fenchene, and on treatment with water was converted completely into *iso*fenchyl alcohol, m. p. 61·5—65°, $[\alpha]_D^{18.5}$ +12·63°. Optical isomerisation must take place during the formation of the chloride. Similar results were obtained with other *iso*fenchyl alcohol preparations.

The remainder of the paper contains a discussion of these results and of Bertram and Helle's observations (*loc. cit.*), together with a criticism of Semmler's views on the constitution of fenchone and its derivatives (*Chem. Zeit.*, 1905, **29**, 1313). G. Y.

Citral. Carl Harries and Alfred Himmelmann (*Ber.*, 1907, **40**, 2823—2826).—In continuation of Harries and Langheld's work (Abstr., 1906, i, 226) the action of ozone on Tiemann's citral *a* and citral *b* (Abstr., 1899, i, 250) has been studied. The two citrals give the same results, which agrees with Tiemann's assumption that they are stereoisomerides. The product of the action of ozone on citral varies with the solvent; in light petroleum solution, Harries and Langheld's ozonide, $C_{10}H_{16}O_5$, but in carbon tetrachloride or glacial acetic acid solution a *diozonide* is formed.

The *diozonide*,  , is obtained as a powder sparingly soluble in carbon tetrachloride; it is only slightly explosive, does not decolorise bromine, and when heated with water yields acetone, lævulaldehyde, and a syrup which is probably glyoxal; the formation of lævulaldehyde peroxide, which is obtained from caoutchouc diozonide, was not observed.

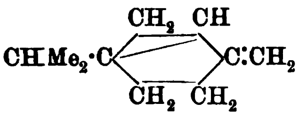
The mono-ozonide decolorises bromine in glacial acetic acid solution and is decomposed by hot water, forming hydrogen peroxide, lævulaldehyde, and acetone peroxide. G. Y.

The Constituents of Ethereal Oils. I. Dihydroterpinene = Carvomenthene. II. Oil from Pilea. III. Addition of Hydrogen Chloride, &c., to Bicyclic Singly Unsaturated Systems. IV. Derivatives of Sabinene and Constitution of Terpinene.

Friedrich W. Semmler (*Ber.*, 1907, **40**, 2959—2968).—*Sabinene monohydrochloride*, $C_{10}H_{16}$,HCl, is obtained, when care is taken to exclude moisture, by passing hydrogen chloride through an ethereal solution of the terpene; b. p. 82—86°/9 mm., D^{20} 0·970, n_D 1·482, a_D −0°15′. The dihydrochloride is formed when moisture is present (compare this vol., i, 145).

On reduction of the monohydrochloride with sodium and alcohol, carvomenthene was obtained, b. p. 57—60°/9 mm., D^{20} 0·8184, n_D 1·4566. To identify the compound it was oxidised by ozone, when a *ketoaldehyde*, $C_{10}H_{18}O_2$, was isolated, b. p. 119—125°/9 mm., D^{20} 0·9439, n_D 1·44962; the *disemicarbazone* has m. p. 183°. On further oxidation of the aldehyde by potassium permanganate, ε-keto-β-*iso*propylheptoic acid, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH(Pr^{\beta})\cdot CH_2\cdot CO_2H$, is obtained, b. p. 174—180°/9 mm., D^{20} 1·019, n_D 1·45662; the phenylhydrazone has m. p. 102° (compare Baeyer, Abstr., 1896, i, 248). The dihydroterpinene gives on treatment with nitrosyl chloride a *bisnitroso-chloride* of m. p. 87°, which yields with benzylamine the *nitrolamine*, $OH\cdot N:C_{10}H_{18}\cdot NH\cdot CH_2Ph$, m. p. 107°.

Menthene gives on oxidation with ozone, *ζ-keto-γη-dimethyloctaldehyde*, $CHMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CHO$, b. p. 122—124°/9 mm., D^{20} 0·959, n_D 1·4483. The identity therefore of the dihydroterpinene with carvomenthene as obtained either from limonene, hydrochloride, or from η- and ψ-phellandrene or sabinene is therefore established (Abstr., 1903, i, 505, 641). The annexed constitution is ascribed to sabinene, and explains the optical activity of the monohydrochloride and the dihydrochloride formation.



The crude oil from *Pilea* has D^{15} 0·8533—0·8520, n_D 1·4686—1·4690, a_D +33°52′—+58°20′. The main fraction has b. p. 167—168°, D^{20} 0·8402, n_D 1·4695, and on oxidation with potassium permanganate gives a glycol, $C_{10}H_{18}O_2$, of b. p. 150—154°/9 mm., D^{20} 1·0332, n_D 1·4852, so that the dicyclic terpine is sabinene.

The author correlates the behaviour of sabinene towards hydrogen chloride with those of camphene and pinene in which new ring systems are produced. W. R.

β-Amyrin Acetate from Balata. N. H. Cohen (*Arch. Pharm.*, 1907, **245**, 245).—α-Balalban (Tschirch and Schereschewski, Abstr., 1905, i, 713) is nothing more or less than β-amyrin acetate.

C. F. B.

Digitoxin. Heinrich Kiliani (*Ber.*, 1907, **40**, 2996—2998).—Cloetta has ascribed to digitoxin the formula $C_{28}H_{46}O_{10}$, and to "digalen" (amorphous digitoxin), $C_{14}H_{23}O_5$ (*Münch. med. Woch.*, 1906, **53**, 2282; 1907, **54**, 987. Compare Kiliani, *ibid.*, 1907, **54**, 886). Crystallised digitoxin is found now to have the molecular weight in chloroform, as determined ebullioscopically, 681 and 582, or in alcoholic solution, 676, and amorphous digitoxin in chloroform, 501, 507, and 515; the formula $C_{34}H_{54}O_{11}$ requires 638, to which these results approximate (compare Abstr., 1899, i, 70). Digitoxin is readily decomposed; when it is boiled for a few minutes with 85% alcohol, the presence of a carbohydrate which reduces Fehling's solution may be detected. Cloetta's "digalen" is considered to have been an impure digitalein. G. Y.

Melanins. Florence M. Durham (*Proc. physiol. Soc.*, 1907, xlvii—xlviii.; *J. Physiol.*, **35**).—The pigments in the hairs of mice are yellow, black, and chocolate; the keratin may be removed either by dissolving it in strong sulphuric acid or stannous chloride. The three pigments, which are associated with a fat-like substance, exhibit certain differences in physical appearance and solubilities.

W. D. H.

Pharmacological Behaviour of Hydroxybenzyltannins. Hermann Hildebrandt (*Arch. Expt. Path. Pharm.*, 1907, **56**, 410—415. Compare Abstr., 1905, i, 153).—Condensation products are readily obtained when an alcoholic solution of a phenol, formaldehyde, and tannic acid is poured into concentrated hydrochloric acid; the condensation consisting in the removal of a nucleus hydrogen atom of the phenol and also of the tannin by the oxygen of the aldehyde.

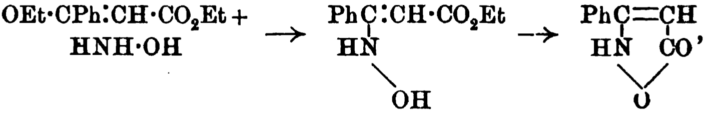
The acetyl and benzoyl derivatives of thymol, anisole, phenetole, and *o*-methoxybenzoic acid also react quantitatively with formaldehyde and tannin. Good yields are also obtained with resorcinol diethyl ether and *β*-naphthol methyl ether, but vanillic acid gives only a poor yield. *p*-Dibromobenzene gives a good yield, but *p*-cymene, benzene, and toluene do not form condensation products. The dibromobenzenemethylenetannin, when distilled with sodium hydroxide solution, yields dibromobenzene. Acetyltannin may also be used in place of tannin.

None of the condensation products which contain alkylated hydroxyl groups possess astringent properties. The carvacrol derivative has the most pronounced pharmacological properties, then follows the thymol derivative, and the effect of the *o*-cresol derivative is not so marked.

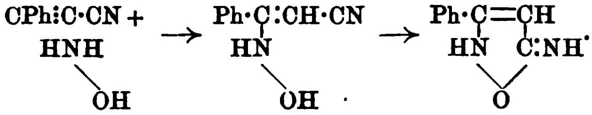
The pharmacological properties of most of the condensation products have been studied, and the question of the relationship between pharmacological properties and constitution is discussed. J. J. S.

Action of Hydroxylamine on Acetylenic Nitriles, Amides, and Esters, and on the Corresponding *β*-Ketonic Compounds.

CHARLES MOUREU and I. LAZENNEC (*Compt. rend.*, 1907, **144**, 1281—1283).—When hydroxylamine in methyl alcoholic solution acts on phenylpropiolonitrile, the substance $C_9H_8ON_2$, m. p. 111°, previously prepared by Obregia by the action of hydroxylamine on benzoylacetonitrile (Abstr., 1892, 324) and by Burns (Abstr., 1893, i, 314), is formed. It gives a *hydrochloride*, m. p. 154—155°, and a *benzoyl* derivative, m. p. 179—180°, and when boiled with concentrated hydrochloric acid forms a substance, $C_9H_7O_2N$, m. p. 151—152° (decomp.), identical with the phenyl*iso*oxazolone prepared by Claisen and Zedel (Abstr., 1891, 468) and Hantzsch (Abstr., 1891, 739) from ethyl benzoylacetate, by Obregia from benzoylacetamide, by Posner (Abstr., 1906, i, 955) from *β*-hydroxylamino-*β*-phenylpropionic acid, and by the authors from the action of free hydroxylamine on ethyl phenylpropiolate, phenylpropiolamide, or ethyl *β*-ethoxycinnamate. Owing to its formation from the latter substance,

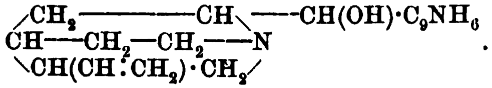


the authors consider that the substance $C_9H_7O_2N$ is 3-phenyl-5-*iso*oxazolone. The reaction with phenylpropiolamide is effected similarly, whilst those with benzoylacetamide and ethyl benzoylacetate can be explained by supposing these substances to act in the enolic form. The compound $C_9H_8ON_2$ must then be 3-phenyl-5-*iso*oxazolonimine, being formed from phenylpropiolonitrile, thus:



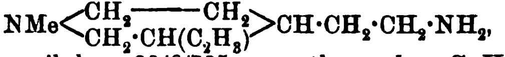
3-Phenyl-5-*iso*oxazolonimine is attacked by nitrous acid, but the product behaves quite differently from that formed by the action of nitrous acid on the amino*iso*oxazole prepared by Hanriot by the action of hydroxylamine on propionylpropionitrile (Abstr., 1892, 79), and the difference in constitution of the two products is probably due to propionylpropionitrile being a substituted, whilst benzoylacetonitrile is a non-substituted, β-ketonic nitrile. The preceding reactions seem to be generally applicable; thus amylpropiolonitrile and hexoylacetonitrile give a *substance*, $C_8H_{14}ON_2$, m. p. 41°, probably amyl*iso*oxazolonimine, which forms a *hydrochloride*, m. p. 104—106°, and an *acetyl* derivative, m. p. 87—88°, and when heated with concentrated hydrochloric acid decomposes into methyl amyl ketone, hydroxylamine and ammonium chlorides, and carbon dioxide, probably owing to a splitting up of the amyl*iso*oxazolone first formed. The latter substance has been obtained in the form of an *ammonium* salt, $C_8H_{12}O_2N{\cdot}NH_4$, m. p. 174—175° (corr. decomp.), and a *benzoyl* derivative, m. p. 72—73°. Similarly, hexylpropiolonitrile and heptoylacetonitrile give a *substance*, m. p. 32°, probably hexyl*iso*oxazolonimine, which forms an *acetyl* compound, m. p. 82·5—83°. The acetylenic and β-ketonic non-substituted nitriles by condensation with hydroxylamines thus give the same cyclic compounds, namely, the *iso*oxazolonimines, whilst the acetylenic amides and esters and the corresponding β-ketonic amides and esters give the same *iso*oxazolones. E. H.

Oximes of 1-Methylcinchotoxine and 1-Methylcinchotintoxine and their Transformation by the Beckmann Reaction. WILHELM KOENIGS [with KARL BERNHART and JOSEF IBELE] (*Ber.*, 1907, **40**, 2873—2882).—It has been shown (this vol., i, 345) that cinchonic acid and 4-aminoquinoline are obtained on hydrolysing the product formed by the Beckmann transformation of the oxime of 1-methylcinchotoxine. It has now been found possible to isolate in addition to these compounds, 4-*aminoethyl*-1-*methyl*-3-*vinylpiperidine* and N-*methylhomomeroquinenine*. The oxime of 1-methylcinchotintoxine behaves in a similar manner, yielding cinchonic acid, 4-aminoquinoline, 4-*aminoethyl*-1-*methyl*-3-*ethylpiperidine*, and N-*methylhomocincholeupone*. From their mode of formation it is probable that these new compounds possess the formulæ assigned to them, although this has not been proved. The author considers Rabe's cinchonine formula (this vol., i, 78) less probable than the one proposed by him some time ago (Abstr., 1900, i, 189), namely,



Rabe, in his last publication (this vol., i, 546), considers it probable that there is present in cinchonine a secondary alcohol group.

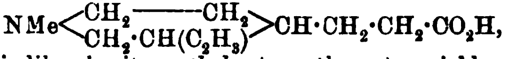
4-*Aminoethyl*-1-*methyl*-3-*vinylpiperidine*,



$$\mathrm{NMe}<\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{CH_2\cdot CH(C_2H_8)}\end{matrix}>\mathrm{CH\cdot CH_2\cdot CH_2\cdot NH_2},$$

is a colourless oil, b. p. 234°/725 mm.; the *oxalate*, $C_{12}H_{22}O_4N_2,H_2O$, forms small needles, m. p. approx. 190° (decomp.); the *aurichloride*, $C_{10}H_{20}N_2,2HAuCl_4,H_2O$, is a crystalline substance, m. p. approx. 102°; the *platinichloride* decomposes at 240°; the *picrate* crystallises in needles; the *tartrate* forms a crystalline powder.

N-*Methylhomomeroquinenine*,



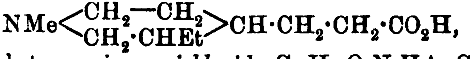
$$\mathrm{NMe}<\begin{matrix}\mathrm{CH_2}\text{———}\mathrm{CH_2}\\ \mathrm{CH_2\cdot CH(C_2H_3)}\end{matrix}>\mathrm{CH\cdot CH_2\cdot CH_2\cdot CO_2H},$$

is an oil, as is likewise its *methyl* ester; the estor yields a crystalline *aurichloride*, $C_{12}H_{21}O_2N,HAuCl_4$, m. p. 122°.

N-*Methylcinchotintoxine*, prepared by Rabe's method from cinchotine methiodide (Arlt, Abstr., 1899, i, 962), is a crystalline substance, m. p. 74—76°; its *oxime*, $C_{20}H_{27}ON_3$, melts at 65—80°.

4-*Aminoethyl*-1-*methyl*-3-*ethylpiperidine*, $C_{10}H_{22}N_2$, yields an *oxalate*, $C_{12}H_{24}O_4N_2,H_2O$, which forms slender needles, m. p. 180—192° (decomp.); the *aurichloride*, $C_{10}H_{22}N_2,2HAuCl_4,H_2O$, crystallises in long needles, m. p. 133—135°; the *platinichloride* forms small, yellowish-red needles, m. p. 250° (decomp.).

N-*Methylhomocincholeupone*,



$$\mathrm{NMe}<\begin{matrix}\mathrm{CH_2}\text{—}\mathrm{CH_2}\\ \mathrm{CH_2\cdot CHEt}\end{matrix}>\mathrm{CH\cdot CH_2\cdot CH_2\cdot CO_2H},$$

is a resinous substance; its *aurichloride*, $C_{11}H_{21}O_2N,HAuCl_4$, is a crystalline substance, m. p. about 120°. The *ethyl* ester is likewise resinous; it yields an *aurichloride*, $C_{13}H_{25}O_2N,HAuCl_4$, obtained as a yellow crystalline powder, m. p. 80—100°. W. H. G.

Action of Halogens on Morphine Derivatives. EDUARD VONGERICHTEN and OTTO HÜBNER (*Ber.*, 1907, **40**, 2827—2831).—The action of halogens on morphine or codeine is totally different from that on α- or β-methylmorphimethine, whereas α- and β-methyldihydromorphimethines behave towards bromine in the same manner as morphine (Vongerichten, Abstr., 1897, i, 643), bromination taking place in the ring carrying the phenolic hydroxyl.

The action of bromine on α-methylmorphimethine in chloroform solution leads to the formation of a *bromohydroxydihydromethylmorphimethine*, $C_{19}H_{24}O_4NBr$, which crystallises in leaflets, m. p. 170°, decomposes with loss of water at about 180°, gives with concentrated sulphuric acid a brownish-red coloration becoming brownish-green and blue on addition of water, and does not give a precipitate with silver nitrate after being heated with dilute sulphuric acid. The crystalline *methiodide* decomposes at about 150°; the *acetyl* derivative, $C_{21}H_{26}O_5NBr$, m. p. 118—138° (decomp.), yields a white, flocculent, tertiary *base* when converted into the *hydrobromide* and treated with ammonia, forms an oily *methiodide*, and on treatment with acetic anhydride is converted into *diacetylmethylthebaol*, m. p. 162°. When heated with acetic anhydride at 180° under pressure, bromohydroxy-α-methyldihydromorphimethine yields a bromomorphol, m. p. 165°.

When heated in a current of hydrogen at 180°, bromo-α-methylmorphimethine, $[\alpha]_D^{15}$ $-104{\cdot}06°$, is transformed into *bromo-β-methylmorphimethine*, $[\alpha]_D^{15}$ $+128{\cdot}22°$. The *methiodide* of this is amorphous and dextrorotatory. *Bromo-α-methylmorphimethine methiodide* has $[\alpha]_D^{15}$ $-110{\cdot}71°$.

Bromo-α-methyldihydromorphimethine, $C_{19}H_{24}O_3NBr$, m. p. 165°, is formed by bromination of α-methyldihydromorphimethine in chloroform or glacial acetic acid solution; the *methiodide*,

$$C_{19}H_{24}O_3NBr,MeI,$$

m. p. 264°, is converted by boiling concentrated sodium hydroxide solution into *bromo-β-methyldihydromorphimethine methiodide*, m. p. 277°. *Bromo-β-methyldihydromorphimethine*, m. p. 169°, is formed by heating the α compound. G. Y.

Pyrrolidone. Julius Tafel and Otto Wassmuth (*Ber.*, 1907, **40**, 2831—2842).—This is a study of the properties of pyrrolidone, which has been easily obtainable since Tafel and Stern prepared it by electrolytic reduction of succinimide (Abstr., 1900, i, 557). The molecular weight of pyrrolidone ($C_4H_7ON = 85$) is found by the vapour density method at 230°/70—80 mm. as 87·3—90·3, but considerably higher, 106—148·5, by the cryoscopic and ebullioscopic methods in benzene solution. Pyrrolidone has both basic and acid properties; with hydrogen chloride and bromide it forms two series of salts containing one equivalent of acid with one and two equivalents respectively of pyrrolidone. The second series belongs to Werner's abnormal ammonium salts (Abstr., 1903, i, 234), and has the general constitution $\begin{matrix}NR_3\\NR_3\end{matrix}\!>\!HX$. This tendency of pyrrolidone to form double molecules appears also in the bromine additive product, $\begin{matrix}NR_3\\NR_3\end{matrix}\!>\!Br{\cdot}Br$. Such formulæ are to be considered as merely schematic. Both series of hydrohaloid salts are strongly dissociated in aqueous solution.

Dipyrrolidone hydrochloride, $(C_4H_7ON)_2,HCl$, crystallises in spears, m. p. 86—88°; *pyrrolidone hydrochloride*, C_4H_7ON,HCl, hexagonal plates, m. p. 128—131°; *dipyrrolidone hydrobromide*, $(C_4H_7ON)_2,HBr$, granular crystals, m. p. 135—137°; *pyrrolidone hydrobromide*,

$$C_4H_7ON,HBr,$$

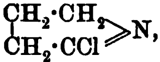
m. p. 108—121°.

The action of bromine on pyrrolidone in chloroform solution leads to the formation of the hydrobromide, 1-bromopyrrolidone, and *pyrrolidone perbromide*; on recrystallisation from chloroform, the bromo-compound remains in solution, the hydrobromide and perbromide separating in mixed crystals. On repeated recrystallisation, the perbromide is transformed gradually into the bromo-compound. The action of acetone on the perbromide, as also on *l*-bromopyrrolidone, leads to the formation of bromoacetone and dipyrrolidone hydrobromide.

1-Bromopyrrolidone is obtained in white crystals if formed in 40% sodium hydroxide solution; it is decomposed by hydrogen iodide forming pyrrolidone, hydrogen bromide, and iodine, or 2 mols. of hydrogen bromide, forming pyrrolidone hydrobromide perbromide, or 1 mol. of hydrogen bromide forming pyrrolidone and bromine.

The *sodium* derivative of pyrrolidone, C_4H_6ONNa, m. p. about 165°, decomposes at higher temperatures. When treated with methyl iodide in benzene solution, it yields 1-*methylpyrrolidone*, C_5H_9ON, which is obtained as a colourless oil, b. p. 197—202°/736 mm., and on hydrolysis forms *γ-methylaminobutyric acid*, $C_5H_{11}O_2N$, m. p. 143—145°, decomposing slightly above its melting point.

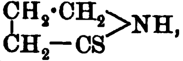
Ethyl pyrrolidone-1-*acetate*, $C_4H_6ON\cdot CH_2\cdot CO_2Et$, formed by the action of ethyl chloroacetate on sodium pyrrolidone, is obtained as an oil, b. p. 280—283°, and on hydrolysis yields *pyrrolidone*-1-*acetic acid*, $C_6H_9O_3N$, crystallising in needles, m. p. 143°; the *potassium* salt has m. p. 209—213°.



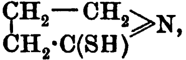
2-*Chloropyrroline*, $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CCl\end{matrix}>N$, prepared by the action of phosphorus pentachloride on pyrrolidone hydrochloride at 85°, crystallises in needles or leaflets, m. p. 50—51°. G. Y.

Thiopyrrolidone. II. Julius Tafel and Paul Lawaczeck (*Ber.*, 1907, **40**, 2842—2848. Compare Abstr., 1905, i, 465).—Thiopyrrolidone, m. p. 116°, is prepared now in a 90% yield by heating pyrrolidone with phosphorus pentasulphide in xylene solution (compare Hantzsch, Abstr., 1889, 723).

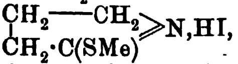
The constitution of thiopyrrolidone is discussed; the sparing solubility in aqueous alkalis and the non-formation of a disulphide point to constitution I, whilst the alkali salts are considered to be derived from II, since their reaction with methyl iodide leads to the formation of ψ-thiopyrrolidone methyl ether, $C_4H_6N\cdot SMe$.

I. 

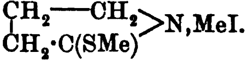
$\begin{matrix}CH_2\cdot CH_2\\ CH_2-CS\end{matrix}>NH$,

II. 

$\begin{matrix}CH_2-CH_2\\ CH_2\cdot C(SH)\end{matrix}>N$,

III. 

$\begin{matrix}CH_2-CH_2\\ CH_2\cdot C(SMe)\end{matrix}>N,HI$,

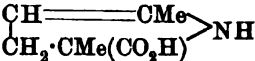
IV. 

$\begin{matrix}CH_2-CH_2\\ CH_2\cdot C(SMe)\end{matrix}>N,MeI$.

The ψ-thio-ether forms a hydriodide, III, and a methiodide, IV, which on treatment with an alkali decomposes, forming 1-methylpyrrolidone and methyl mercaptan.

Thiopyrrolidone methiodide, $C_5H_{10}NSI$, crystallises in yellow needles, m. p. 139°, and when treated with concentrated potassium hydroxide yields *methyl-ψ-thiopyrrolidone*, $C_4H_6N\cdot SMe$, which is formed also by the action of methyl iodide on potassium thiopyrrolidone. The *methyl ether* is obtained as a colourless, highly refracting, alkaline oil, b. p. 170°/755 mm., and has an odour of mercaptan and pyrrolidine. On reduction with zinc dust and acetic acid, or electrolytically in sulphuric acid solution with a current density of 2·4 amperes, it yields methyl mercaptan and pyrrolidine. When oxidised with potassium permanganate in aqueous solution, the methyl ether yields potassium methanesulphonate and pyrrolidone. The *methiodide*, $SMe\cdot C_4H_6N,MeI$, crystallises in needles, m. p. 122°. G. Y.

Synthesis of a Pyrrolinecarboxylic Acid. Nicolai Zelinsky and N. Schlesinger (*Ber.*, 1907, **40**, 2886—2888. Compare Abstr., 1906, i, 425).—The nitriles of α-amino-acids have been synthesised by the action of potassium cyanide and ammonium chloride on diketones.

2 : 5-*Dimethylpyrroline-5-carboxylic acid*,  $\begin{matrix}\mathrm{CH} = \mathrm{CMe} \\ | \\ \mathrm{CH_2 \cdot CMe(CO_2H)}\end{matrix}\!\!>\!\mathrm{NH}$, has been obtained from the condensation product of acetonylacetone and potassium cyanide. The *copper* salt, $(C_7H_{10}O_2N)_2Cu$, separates from alcohol in pale blue crystals; the neutral solution of the salt is not affected by hydrogen sulphide, but in the presence of hydrochloric acid an immediate precipitate is formed. The *hydrochloride* of the amino-acid is extremely readily soluble in water or alcohol and crystallises in long needles.

The primary condensation product has b. p. 108°/17 mm., and consists of a mixture of the ketonic nitrile,

$$CN \cdot CMe(NH_2) \cdot CH_2 \cdot CH_2 \cdot COMe,$$

and of the nitrile of the pyrrolinecarboxylic acid. From the mixture, the *semicarbazone*, $C_8H_{15}ON_5$, of the amino-keto-nitrile has been isolated. J. J. S.

Chloro- and Bromo-Columbates and Chlorotantalates.

RUDOLF F. WEINLAND and LUDWIG STORZ (*Zeitsch. anorg. Chem.*, 1907, **54**, 223—243).—The first part of the paper contains a detailed account of the preparation and properties of chloro- and bromo-columbates of the types $CbOX_3,RX$ and $CbOX_3,2RX$ ($R =$ alkali metal or organic base, $X = Cl$ or Br) which have been already described (Abstr., 1906, ii, 764). Attempts to prepare corresponding iodo-derivatives were unsuccessful owing to the insolubility of columbic acid in concentrated hydriodic acid. The so-called double columbium pyridine iodide described by Renz (Abstr., 1903, i, 774) appears to have been pyridine periodide, $C_5H_6NI_2$.

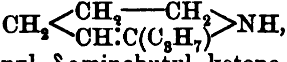
The following tantalum double salts with pyridine and quinoline were prepared by the action of the base on tantalum pentachloride dissolved in alcohol containing hydrogen chloride: $TaOCl_3,2C_5H_6NCl,2C_2H_6O$; $2TaOCl_3,3C_5H_6NCl,2C_2H_6O$;

$$Ta_2O_2Cl_4,4C_5H_6NCl,$$

and $TaOCl_3,2C_9H_8NCl,2C_2H_6O$. The first pyridine double salt was obtained from solutions free from water, the second and third from solutions containing increasing amounts of water. All the compounds form colourless crystals soluble in alcohol, but decomposed by water; they gradually become opaque on exposure to the air.

Attempts to prepare bromotantalates were unsuccessful owing to the insolubility of tantalum bromide in hydrogen bromide. G. S.

Which Substances contain a Readily Resolvable, Single Carbon-Nitrogen Linking?

ERNST MOHR (*J. pr. Chem.*, 1907, [ii], **75**, 549—555).—von Braun and Steindorff have shown that γ-coniceine,  $\mathrm{CH_2}\!<\!\begin{matrix}\mathrm{CH_2 - CH_2} \\ \mathrm{CH{:}C(C_8H_7)}\end{matrix}\!>\!\mathrm{NH}$, readily undergoes hydrolysis, forming propyl δ-aminobutyl ketone, $NH_2 \cdot [CH_2]_4 \cdot CO \cdot C_8H_7$ (Abstr., 1905, i, 812). The present paper is a discussion of the question: is the C–N linking in the grouping $C{:}C \cdot N$ or $X{:}C \cdot N$ always unstable or only so in particular cases? The conclusion is drawn that no general rule can be laid down, since whilst the linking in question is readily resolved in many substances, in others, such as aniline, it is extremely stable. Between these extremes are substances which contain the grouping and in which are found all degrees of stability of the C–N linking. Thus there are amides which are hydrolysed with great ease, others in which the hydrolysis is normal, and finally those which can be hydrolysed only with difficulty. G. Y.

An Optically Active Tetrahydroquinoline Compound.

F. BUCKNEY (*Proc. Camb. Phil. Soc.*, 1907, **14**, 177—178. Compare Wedekind, Abstr., 1905, i, 520).—It has been found possible to effect the resolution of allylkairolinium iodide into the two optically active forms, the salts, d-*allylkairolinium* d-*bromocamphorsulphonate* and l-*allylkairolinium* d-*bromocamphorsulphonate*, having been isolated. This is the first case of an optically active compound in which the activity is due to a nitrogen atom in a ring.

Allylkairolinium iodide, $C_{13}H_{18}NI$, prepared by adding allyl iodide to kairoline (methyltetrahydroquinoline), forms small, yellow, prismatic crystals, m. p. 130°.

Allylkairolinium d-*bromocamphorsulphonate*, $C_{23}H_{32}O_4NBrS$, prepared by the interaction of the silver salt of the acid with the above iodide, yields, when repeatedly crystallised from a mixture of ethyl acetate and a little toluene, two kinds of crystals : small, colourless, transparent crystals sparingly soluble in ethyl acetate, m. p. 164°, and silky needles readily soluble in ethyl acetate, m. p. 153·5°. The less soluble salt is evidently the *l*-base *d*-acid salt, since it gives $[\alpha]_D$ +39·1° and $[M]_D$ +195°, so that the basic ion, $C_9H_{10}NMe{\cdot}C_3H_5$, has the value $[M]_D$ −75°. The more soluble compound is the *d*-base *d*-acid salt, since it gives $[\alpha]_D$ +68·6° and $[M]_D$ +342°, whence the value of $[M]_D$ for the basic ion is +72°.

The iodides could not be recovered from the *d*-bromocamphorsulphonates, being too soluble in water. W. H. G.

Catalytic Action of Finely-divided Metals on Nitrogen Compounds.

MAURICE PADOA and UGO FABRIS (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 921—924. Compare this vol., i, 636).—The action of finely-divided nickel and hydrogen on acridine vapour at 250°—270° yields 2 : 3-dimethylquinoline (compare Rohde, Abstr., 1887, 974) and not a methylated carbazole, which would be expected if the change were analogous with that occurring in the case of quinoline (see Padoa and Carughi, Abstr., 1906, i, 765). T. H. P.

Conductivities of the Isomeric Hydrogen Esters of Quinolinic and Cinchomeronic Acids.

ALFRED KIRPAL (*Monatsh.*, 1907, **28**, 439—445).—With the object of determining the strength of the two carboxyl groups in quinolinic acid and cinchomeronic acid, electrical conductivity measurements of the hydrogen esters of the acids have been made.

2-Methyl 3-hydrogen quinolinate is not hydrolysed even in very dilute aqueous solutions; it has a conductivity constant, $k=0·265$. 3-Methyl 2-hydrogen quinolinate has a conductivity, $k=0·138$. From these values it is evident that the 3- or β-carboxyl group is stronger than the 2- or α-carboxyl group, so that, employing the nomenclature proposed by Wegscheider (Abstr., 1903, i, 146), 2-methyl 3-hydrogen quinolinate is the *b*-ester acid, whilst the isomeride is the *a*-ester acid.

Since quinolinic anhydride, when treated with methyl alcohol, is converted into 80% of the *b*-methyl ester acid, it follows that quinolinic acid does not follow Wegscheider's rule for the esterification of dibasic acids (Abstr, 1895, ii, 310; 1898, i, 238), for the weaker 2- or α-carboxyl group undergoes esterification more readily than the stronger 3- or β-carboxyl group.

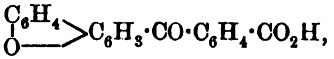
γ-Methyl cinchomeronate has a conductivity $k = 0{\cdot}0665$, whilst the β-methyl ester has the conductivity $k = 0{\cdot}0666$, from which it follows that the two carboxyl groups have practically the same electrolytic dissociation constant. It would therefore be expected that equal quantities of the two esters would be obtained from the acid anhydride, but this is not the case, so that Wegscheider's rule is inapplicable likewise to cinchomeronic acid.

It is probable that this abnormal behaviour is due to the influence of the nitrogen atom. W. H. G.

Condensation Products of Carbazole and Diphenylene Oxide with Phthalic Anhydride. RUDOLF STÜMMER (*Monatsh.*, 1907, **28**, 411—422).—An investigation of the two compounds prepared originally by Goldschmiedt and Lipschitz (Abstr., 1905, i, 132) by the condensation of phthalic anhydride with carbazole and diphenylene oxide, but not investigated by these authors.

Carbazole-N-*carbonyl*-o-*benzoic acid*, $C_{12}H_8N\cdot CO\cdot C_6H_4\cdot CO_2H$, prepared by the action of phthalic anhydride on carbazole in carbon disulphide solution in presence of aluminium chloride, crystallises from alcohol in white, rhombic plates; it sinters at 150°, m. p. 190°, at which temperature it dissociates into its components. The solution in concentrated sulphuric acid is colourless. The amorphous *silver* salt decomposes at 146°. The *methyl* ester, $C_{21}H_{15}O_3N$, prepared by the action of methyl iodide on the silver salt, forms small crystals, m. p. 194—201° (decomp.). The *amide*, $C_{20}H_{14}O_2N_2$, obtained when ammonia acts on the acid chloride prepared by means of thionyl chloride, crystallises from pyridine in small, white plates, m. p. 235—238° (decomp.).

o-*Diphenylene-oxide-ketobenzoic acid*,



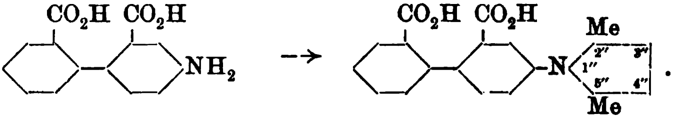
$\left.\begin{matrix}C_6H_4\\|\\O\end{matrix}\right>C_6H_3\cdot CO\cdot C_6H_4\cdot CO_2H$,

formed when a solution of phthalic anhydride and diphenylene oxide in light petroleum is treated with aluminium chloride, crystallises from methyl alcohol in small, colourless plates, m. p. 208—210°. The *methyl* ester, $C_{21}H_{14}O_4$, obtained by treatment of the silver salt with methyl iodide, by esterification with alcohol and sulphuric acid, or by treatment of the acid chloride prepared by phosphorus trichloride with methyl alcohol, forms small, thin plates, m. p. 99—103°, and dissolves in concentrated sulphuric acid to a yellowish-red solution. The isomeric *methyl* ester, prepared by the action of methyl alcohol on the acid chloride obtained by means of thionyl chloride, forms an amorphous, white powder, m. p. 72—105° after sintering at 55°. It dissolves, as does the free acid, in concentrated sulphuric acid to an intense dark red solution. The *amide*, $C_{20}H_{13}O_8N$, formed when ammonia acts on the acid chloride, is a white powder, m. p. 115—118°. The *oxime anhydride*, $C_{20}H_{11}O_8N$, obtained by the action of free hydroxylamine on the acid in excess of potassium hydroxide, crystallises in colourless needles, m. p. 203—206°. The *phenylhydrazone anhydride*, $C_{28}H_{16}O_2N_2$, prepared by the interaction of the acid and phenylhydrazine, forms colourless plates, m. p. 221—223°.

W. H. G.

Syntheses of Pyrrole Derivatives of High Molecular Weights. Julius Schmidt and Richard Schall (*Ber.*, 1907, 40, 3002—3011).—The authors have previously described (Abstr., 1906, i, 23) the preparation of 6-amino-, 4-amino-, 6 : 6′-diamino-, and 4 : 4′-diamino-diphenic acids. Since certain naturally occurring compounds contain the pyrrole nucleus, the authors have utilised the acids in question in order to add on the diphenyl group to the pyrrole ring by interaction of the reactive amino-groups with γ-diketo-compounds.

4-Aminodiphenic acid, (I), for example, combines with acetonyl acetone to form 2″ : 5″-dimethyl-4-pyrrolediphenic acid, (II):



(I.) (II.)

The influence of steric retardation was noted in certain cases. Thus, whilst 4-amino- and 4 : 4′-diamino-diphenic acids readily form pyrrole derivatives, such derivatives could not be obtained from 6-amino-, 6 : 6′-diamino-, and 6-amino-6′-hydroxy-diphenic acids.

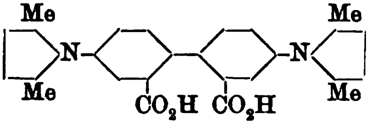
The diketones used were acetonylacetone and ethyl β-diacetylsuccinate. Pyrrole derivatives were not obtained when ethyl dibenzoylsuccinate was used. This is an instructive example of the fact that the reactivity of carbonyl groups is influenced by the groups attached to them.

Not only the pyrrole derivatives obtained, but also the aminodiphenic acids used in their preparation gave the so-called pyrrole reaction, causing pine-wood shavings moistened with hydrochloric acid to assume a red colour. This reaction, accordingly, is not so very trustworthy as a characteristic test for pyrrole compounds.

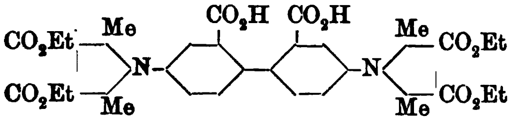
2″ : 5″-*Dimethyl-4-pyrrolediphenic acid*, (II), when first prepared, is white, but is readily changed by air, assuming a red tint. It decomposes at 100—115°.

3″ : 4″-*Dicarbethoxy-2″ : 5″-dimethyl-4-pyrrolediphenic acid*, obtained from *p*-aminodiphenic acid and ethyl β-diacetylsuccinate, forms white needles, m. p. 229—230°. When saponified, it yields the corresponding *acid*, $C_{22}H_{17}O_8N,H_2O$, which separates from dilute alcohol in colourless needles, m. p. 239—240°.

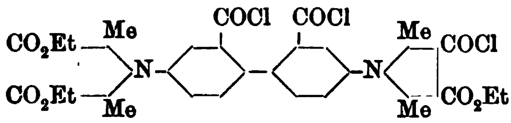
2″ : 5″-2‴ : 5‴-Tetramethyl-4 : 4′-dipyrrolediphenic acid, obtained by the condensation of 4 : 4′-diaminodiphenic acid with acetonylacetone, crystallises in leaflets, m. p. 284—285° (decomp.).



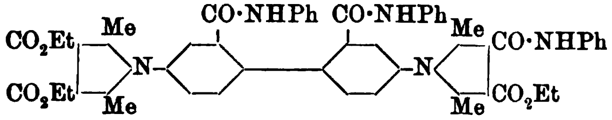
3″ : 4″ : 3‴ : 4‴-Tetracarbethoxy-2″ : 5″ : 2‴ : 5‴-tetramethyl-4 : 4′-dipyrrolediphenic acid, obtained from 4 : 4′-diaminodiphenic acid and ethyl β-diacetylsuccinate, crystallises in colourless leaflets, m. p. 285—286° (decomp.). When saponified, it forms the corresponding *acid*, $C_{30}H_{24}O_{12}N_2,2H_2O$, m. p. 234—235° (decomp.).



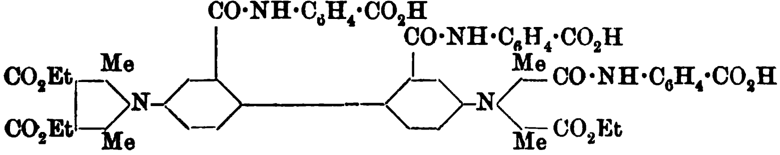
When the tetracarbethoxy compound is warmed with an excess of phosphorus pentachloride, one carbethoxyl group only is attacked; the resulting *trichloride* has m. p. 175—177° and is comparatively stable towards water and alcohol. The corresponding *triamide* has m. p. 120—130° (decomp.).



The trichloride combines with amino-compounds in a manner comparable with the formation of polypeptides by combination of amino-acids with chlorides of amino-acids. With aniline it forms the *trianilide*, which is a colourless, amorphous powder, decomposing at about 130°.

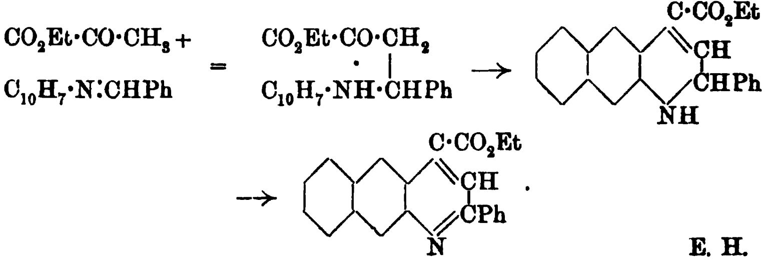


When condensed with *p*-aminobenzoic acid, the trichloride forms the *compound* which is an amorphous powder decomposing at 160—170°.

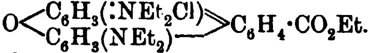


A. McK.

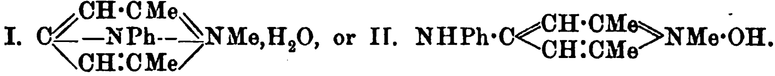
Mechanism of the Synthesis of Quinoline Derivatives (Döbner's Reaction). Louis J. Simon and Charles Mauguin (*Compt. rend.*, 1907, **144**, 1275—1278).—By using chloroform or benzene instead of alcohol in the condensation of β-naphthylamine with pyruvic acid and benzaldehyde, and also by acting on pure benzylidene-β-naphthylamine (1 mol.) with pyruvic acid (1 mol.), the authors have obtained methyl-, phenyl-, and tetrahydrophenylnaphthaquinolinecarboxylic acids, benzylnaphthylamine, and a constant excess of benzaldehyde. It is evident therefore that the hydrogen liberated in Döbner's reaction is used up in reducing part of the benzylidenenaphthylamine and the phenylnaphthaquinolinecarboxylic acid. Moreover, this removal of part of the benzylidenenaphthylamine from the sphere of action leaves the pyruvic acid in excess, and thus explains the formation of methylnaphthaquinolinecarboxylic acid and the excess of benzaldehyde remaining. The authors could not isolate the dihydro-acid, which is probably formed as an intermediate product, but by replacing the pyruvic acid by ethyl pyruvate they have isolated a small quantity of the additive product, and by transforming it into ethyl phenylnaphthaquinolinecarboxylate they show that the course of the reaction must be represented by:


$CO_2Et\cdot CO\cdot CH_3$ +
$C_{10}H_7\cdot N\colon CHPh$
=
$CO_2Et\cdot CO\cdot CH_2$
$C_{10}H_7\cdot NH\cdot CHPh$
C·CO₂Et
CH
CHPh
NH
C·CO₂Et
CH
CPh
N

E. H.

Alkali Salts of Rhodamines. LEONHARD WACKER (*Zeitsch. Farb. Ind.*, 1907, 6, 201—203).—Bernthsen has shown (*Chem. Zeit.*, 1892, 16, 1956—1957; D.R.-P., 73573) that the compound obtained by Monnet (Abstr., 1893, i, 274) by the esterification of tetraethylrhodamine is not, as this author supposed, a diethoxy-compound, but a monoethyl ester, the hydrochloride of which probably has the formula:  $O<\begin{matrix}C_6H_3(\colon NEt_2Cl)\\C_6H_3(NEt_2)\end{matrix}>C_6H_4\cdot CO_2Et$. The author has been able to obtain the *sodium* salt, corresponding with this ester, by adding a hot solution of tetraethylrhodamine in water containing an excess of hydrochloric acid to an aqueous sodium hydroxide solution, 48°Bé. The sodium salt separates as a scarlet precipitate which becomes violet after a time; on heating the solution to $80-90°$, the scarlet precipitate turns cornflower-blue and becomes crystalline. The dry salt is a dark blue, almost black, powder. In aqueous solution, it is probably hydrolysed into the free acid and sodium hydroxide, for although stable at the ordinary temperature, the solution decomposes when heated with separation of the lactone of the acid. The *potassium* salt, likewise the *sodium* and *potassium* salts of *s*-diethylrhodamine, may be prepared in the same way. None of the salts described was analysed. W. H. G.

Methylanilinolutidine. AUGUST MICHAELIS and OTTO HILLMANN (*Annalen*, 1907, 354, 91—101. Compare Michaelis and Hölken, Abstr., 1904, i, 774; Fischer and Demeler, Abstr., 1899, i, 635).—As Michaelis and Hölken found that the two halogen atoms of 4-chlorolutidine methiodide could be substituted by an atom of sulphur or selenium, it seemed of interest to determine if the action of aniline on 4-chlorolutidine would lead to the formation of the oxygen-free base, methylanilolutidine. The base, obtained on treating the immediate product of the reaction with an alkali, contains a stable molecule of water and may have either of the two constitutions:



$$\text{I. } C\left\{\begin{matrix}\text{CH·CMe}\\ \text{—NPh—}\\ \text{CH:CMe}\end{matrix}\right\}NMe,H_2O, \text{ or II. } NHPh\cdot C<\substack{CH\cdot CMe\\ CH:CMe}>NMe\cdot OH.$$

In favour of I. is the addition of methyl iodide with formation of water and 4-anilino-*N*-methyl-lutidine at the ordinary temperature, as also the liberation of the base from its salt by alkalis, whereas the strong alkaline reaction of the base, its insolubility in ether, and the stability of the mol. of water, which cannot be removed without destruction of the whole molecule, point to constitution II. The authors consider that the product of the action of aniline on 4-chlorolutidine methiodide is the hydriodide of the base I., and that this base on liberation by an alkali immediately combines with water, forming the ammonium hydroxide base, II. When heated, the *methiodide*,

$$NMePh\cdot C<\substack{CH:CMe\\ CH\cdot CMe}>NMeI,$$

formed by the action of methyl iodide on the base I. or II., yields 4-*methylanilinolutidine*, $NMePh\cdot C<\substack{CH:CMe\\ CH\cdot CMe}>N$, which is isomeric with the base I. This combines with water forming an ammonium hydroxide base, $NMePh\cdot C<\substack{CH:CMe\\ CH\cdot CMe}>NH\cdot OH$, which has a strong alkaline reaction and is insoluble in ether, but differs from the first ammonium hydroxide base in that it loses water readily over sulphuric acid in a desiccator. These results agree with Michaelis's view that the alkaline reaction of the iminopyrines in aqueous or aqueous-alcoholic solution must be ascribed to the formation of ammonium hydroxide bases (Abstr., 1905, i, 476).

4-Anilinolutidine methiodide, obtained by the action of aniline on 4-chlorolutidine methiodide or of methyl iodide on 4-anilinolutidine (Conrad and Epstein, Abstr., 1887, 501), forms large, colourless needles, m. p. 223°.

4-*Anilino*-N-*methyl-lutidinium hydroxide* forms small, yellowish-white needles, m. p. 115°, and is stable at 110° in a current of hydrogen; the *hydrochloride*, $C_{14}H_{16}N_2,HCl$, forms colourless, hygroscopic needles; the *platinichloride*, $(C_{14}H_{16}N_2)_2,H_2PtCl_6$, crystallises in yellow prisms, m. p. 218°; the *aurichloride* forms red needles, m. p. 159°; the *mercurichloride*, white plates, m. p. 175°; the *thiocyanate*, $C_{14}H_{16}N_2,HCNS$, m. p. 172°; the *picrate*, greenish-yellow leaflets, m. p. 178°.

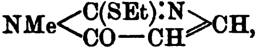
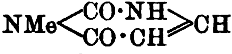
4-*Methylanilinolutidine methiodide* crystallises in white leaflets, m. p. 166°; the *methochloride* forms a white, hygroscopic, crystalline mass. 4-*Methylanilinolutidine* is obtained as a colourless oil, b. p. 263—265°, which absorbs water, forming the *ammonium hydroxide base*, m. p. 75°. The *hydrochloride*, (H_2O), m. p. 214°, *platinichloride*, $(C_{14}H_{16}N_2)_2,H_2PtCl_6$, yellowish-red needles, m. p. 208°, *aurichloride*, $C_{14}H_{16}N_2,HAuCl_4$, red crystals, m. p. 118°, *mercurichloride*, plates, m. p. 126°, *thiocyanate*, white needles, m. p. 145°, and *picrate* were analysed. G. Y.

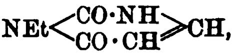
Piperazine and αε-Dihalogen-pentanes. JULIUS VON BRAUN (*Ber.*, 1907, **40**, 2935—2937).—Owing to the tendency of αε-dibromopentane to form a piperidine ring, the action of secondary bases on this substance or on the corresponding di-iodo-compound proceeds in this manner, to the exclusion of pentamethylene derivatives of the type $HBr\cdot NR_2\cdot[CH_2]_5\cdot NR_2HBr$ (this vol., i, 151).

Di-iodopentane and piperazine when heated on the water-bath combine together and give Aschan's diethylenedipiperidyl iodide (Abstr., 1899, i, 542); the dibromopentane reacts more sluggishly, giving the corresponding bromide (Brühl, *Ber.*, 1874, **4**, 738).

W. R.

Pyrimidines. XX. Some Condensation Products of a Substituted ψ-Thiocarbamide. Synthesis of 1-Methyluracil. TREAT B. JOHNSON and FREDERICK W. HEYL (*Amer. Chem. J.*, 1907, **37**, 628—637).—It has been shown previously (Wheeler and Merriam, Abstr., 1903, i, 524; Wheeler and Johnson, Abstr., 1904, i, 624; Wheeler and Bristol, Abstr., 1905, i, 482) that ψ-thiocarbamides undergo condensations more readily than the normal thiocarbamides. In the present paper, an account is given of the behaviour of a monosubstituted ψ-thiocarbamide towards some ketonic esters. It is found that condensation occurs with the formation of substituted thiolpyrimidines, which are converted by hydrochloric acid into uracil derivatives.

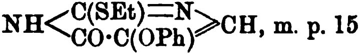
ψ-Methylethylthiocarbamide hydriodide, $NHMe\cdot C(SEt){:}NH,HI$, obtained by the action of ethyl iodide on methylthiocarbamide, is an extremely hygroscopic solid. When this salt is treated with ethyl sodioformylacetate in presence of potassium hydroxide, it is converted into 6-*oxy*-2-*ethylthiol*-1-*methylpyrimidine*,  $NMe<\substack{C(SEt){:}N\\ CO-CH}>CH$, m. p. 79—80°, which forms stout prisms. This compound is also produced by the action of methyl iodide on 6-oxy-2-ethylthiolpyrimidine (Wheeler and Merriam, *loc. cit.*). 2 : 6-*Dioxy*-1-*methylpyrimidine* (1-*methyluracil*),  $NMe<\substack{CO\cdot NH\\ CO\cdot CH}>CH$, m. p. 174—175°, crystallises in microscopic prisms, and when treated with a mixture of nitric and sulphuric acids is converted into 5-nitro-2 : 6-dioxy-1-methylpyrimidine (Behrend and Thurm, Abstr., 1902, i, 832). The corresponding 5-*bromo*-derivative, m. p. 228—229°, forms transparent prisms.

2 : 6-*Dioxy*-1-*ethylpyrimidine* (1-*ethyluracil*),  $NEt<\substack{CO\cdot NH\\ CO\cdot CH}>CH$, m. p. 173—174°, prepared by treating 6-oxy-2-ethylthiolpyrimidine with ethyl iodide in presence of potassium hydroxide and heating the product with strong hydrochloric acid, crystallises in prisms.

When 2-ethylthiol-1 : 4-dimethylpyrimidine, obtained by the condensation of ψ-methylethylthiocarbamide with ethyl acetoacetate, is boiled with concentrated hydrochloric acid, 2 : 6-dioxy-1 : 4-dimethylpyrimidine (Behrend and Thurm, *loc. cit.*) is produced.

By the action of sodium ethoxide on a mixture of ethyl phenoxyacetate and ethyl formate, the *sodium* derivative of ethyl β-hydroxy-α-phenoxyacrylate, $ONa\cdot CH:C(OPh)\cdot CO_2Et$, is formed, which when treated with sulphuric acid yields the *ethyl* ester as a heavy oil. The *hydrazone* of ethyl formylphenoxyacetate,

$$NHPh\cdot N:CH\cdot CH(OPh)\cdot CO_2Et,$$

m. p. 219—221° (decomp.), forms yellow prisms. 6-*Oxy*-5-*phenoxy*-2-*ethylthiolpyrimidine*,  $NH\left<\begin{matrix}C(SEt)=N\\CO\cdot C(OPh)\end{matrix}\right>CH$, m. p. 159°, obtained by condensing ψ-ethylthiocarbamide with the sodium derivative of ethyl β-hydroxy-α-phenoxyacrylate, crystallises in transparent prisms.

E. G.

New Method of Preparation of Azoimide and Diazobenzeneimide [Phenylazoimide].

August Darapsky (*Ber.*, 1907, **40**, 3033—3039. Compare Dimroth, this vol., i, 652).—The author has extended the study of the action of sodium hypochlorite and hypobromite on amides to amino-substances containing three or four nitrogen atoms in the chain in the hope of obtaining triazans or butylene derivatives. Biuret, however, gave hydrazine, and semicarbazide was completely decomposed with evolution of nitrogen in the cold. Hydrazodicarbonamide or azodicarbonamide are partly converted into triazencarbonamide, $NH_2\cdot CO\cdot N:N\cdot NH_2$, which was not isolated, but converted into sodium azoimide by oxidation and hydrolysis. The yield was about 9%.

Phenylsemicarbazide or phenylazocarbonamide give 53% and 64% yields of phenylazoimide accompanied by the formation of a small quantity of azobenzene. That phenyltriazen is an intermediate product in this reaction is proved by obtaining the compound by reducing phenylazoimide in ether at −20° with stannous chloride, and is quantitatively oxidised again to phenylazoimide by hypobromite. The semicarbazides or azocarbonamides from *p*-methyl-, *p*-nitro-, and *p*-bromo-phenylhydrazine, and β-naphthylhydrazine all yield azoimides as the chief product of the reaction. Benzylsemicarbazide or benzoylsemicarbazide are not converted into azoimides, neither are they oxidised by permanganate to azocarbonamides. The conclusion is drawn that only such derivatives of hydrazinecarbonamides as are capable of being oxidised to azocarbonamides can be converted into azoimides by hypochlorite.

Benzoylhydrazine under the same conditions gives benzaldehydebenzoylhydrazone.

W. R.

New Compound Obtained by the Action of Iodine on Benzaldehydephenylhydrazone in Pyridine Solution. II.

Giovanni Ortoleva (*Atti R. Accad. Lincei*, 1907, [v], **16**, i, 874—884. Compare Abstr., 1906, i, 715).—Various new derivatives of the compound $C_{18}H_{14}N_3I$ (*loc. cit.*) are described, and its salt-like character confirmed.

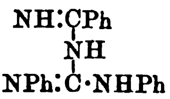
The *nitrate*, $C_{18}H_{13}N_3,HNO_3$, prepared by the action of nitric acid on the hydriodide, forms white needles, m. p. 214—215°. The *platinichloride*, $(C_{18}H_{13}N_3)_2,H_2PtCl_6$, m. p. 238—239°; the *perbromide*, $C_{18}H_{13}N_3,HBr,Br_2$, red needles, m. p. 161—162° or, when crystallised from alcohol, 147—148°, and the *picrate*, $C_{18}H_{13}N_3,C_6H_3O_7N_3$, m. p. 185—187°, were also prepared.

The base, $C_{12}H_9N_3$, obtained by oxidising the hydriodide, $C_{18}H_{13}N_3,HI$, with permanganate, yields the following derivatives. The *hydrochloride*, $C_{12}H_9N_3,HCl$, m. p. 181—182°; the *compound* $C_{12}H_9N_3,3HgCl_2,2H_2O$, m. p. indefinite; the *platinichloride*, $(C_{12}H_9N_3)_2,H_2PtCl_6,2\frac{1}{2}H_2O$, which, when heated at 180—200°, yields the platinosochloride, $(C_{12}H_8N_3)_2,PtCl_2$; the *picrate*, $C_{12}H_9N_3,C_6H_3O_7N_3$, m. p. 160—161°; the *ethiodide*, $C_{12}H_9N_3,EtI$, m. p. 189—190°, and the *compounds* $C_{12}H_9N_3,2BzCl$, m. p. 183—186°, and $C_{12}H_9N_3,AcCl$, m. p. 183—185°.

Oxidation of the hydriodide, $C_{13}H_{18}N_3,HI$, with permanganate in acid solution yields: (1) an *acid*, $C_{12}H_{10}O_2N_2$, m. p. 114—115°, and (2) a substance, m. p. 143—145°, which gives a red coloration with ferric chloride. T. H. P.

Two New Classes of Metallic Salts of Imino-bases. Theory of Internally Complex Metallic Salts. HEINRICH LEY and F. MÜLLER (*Ber.*, 1907, 40, 2950—2958. Compare this vol., i, 301).—The salts of diguanides have been investigated as being related to the acid imides, and, in order to ascertain which groups in the molecule of these compounds are necessary in order that the central hydrogen atom should still be replaceable by a metal, the 2 : 4 : 5-triphenylguanylamidide and 2 : 4 : 5-triphenylamidide have been prepared. These compounds are bases yielding hydrochlorides not hydrolysed in aqueous solution, and also stable abnormally coloured salts of heavy metals.

2 : 4 : 5-*Triphenylguanylamidide*, prepared by mixing a dry ethereal solution of benzamidine (1 mol.) with carbodiphenylimide (1 mol.), crystallises from alcohol in pale yellow needles, m. p. 142°. The *hydrochloride*, m. p. 252° (decomp.), is colourless, as is also the *sulphate*. The *cobalt* salt is deep yellow, that of *copper* is pale yellowish-grey, and the *nickel* salt is flesh-coloured. The base on hydrolysis gives diphenylguanidine; on warming the base with acetic anhydride, it is converted into a *triazine* compound, $C_{22}H_{18}N_4$, which crystallises in yellow leaflets, and, although forming a hydrochloride, does not form salts with metals. A *compound*, $C_{33}H_{28}N_6$, is formed as a by-product in the preparation of triphenylguanylamidide. It has m. p. 236°, is lemon-yellow in colour, and gives a hydrochloride, but no metallic salts. It possesses great stability, and is probably a cyclic compound.

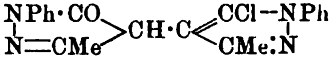


$$\begin{array}{l}NH{:}CPh\\ \quad\ |\\ \quad NH\\ \quad\ |\\ NPh{:}C{\cdot}NHPh\end{array}$$

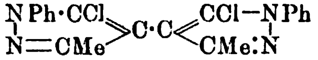
2 : 4 : 5-*Triphenyldiamidide*, $NH{:}CPh{\cdot}NH{\cdot}CPh{:}NPh$, obtained by the interaction of benzamidine (2 mols.) with benzanilinoiminochloride (1 mol.), forms pale yellow crystals, m. p. 152°. The *hydrochloride*, m. p. 250° (decomp.), is colourless. The *copper* salt is brown, the *nickel* and *cobalt* salts yellow.

The authors discuss the nature of these salts from the point of view of Werner's theory. W. R.

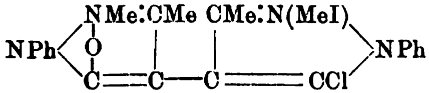
Pyrines from Bis-1-phenyl-3-methyl-5-pyrazolone. AUGUST MICHAELIS, OTTO RADEMACHER, and ENOCH SCHMIEDEKAMPF (*Annalen*, 1907, **354**, 55—90. Compare Abstr., 1905, i, 476).—In continuation of the study of pyrines, the preparation of such substances from a bispyrazolone offered some points of interest, since the presence of the two pyrazole nuclei afforded the possibility of forming, on the one hand, bispyrines and, on the other, mixed pyrines. This has been accomplished as follows. Bis-1-phenyl-3-methyl-5-pyrazolone yields two *derivatives* when heated with phosphorus oxychloride in a sealed tube: (I) at 140—150°; (II) at 170°. The first of these is soluble in alkalis, and is converted by methyl iodide, or methyl sulphate and potassium iodide, into a *substance*, (III), which is a derivative of antipyrine and at the same time a 5-chloropyrazole methiodide. On treatment with potassium hydrogen sulphide, ammonia, or aniline, it yields the mixed pyrines, *antithiopyrine*, (IV), *anti-iminopyrine*, (V), and *antianilopyrine*, (VI), respectively.

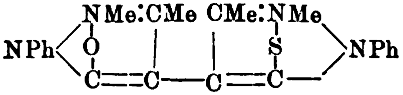
I.


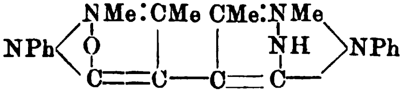
$$\begin{matrix}\mathrm{NPh\cdot CO} \\ \mathrm{N{=}CMe}\end{matrix}\!\!>\!\mathrm{CH\cdot C}\!<\!\!\begin{matrix}\mathrm{CCl{-}NPh} \\ \mathrm{CMe{:}N}\end{matrix}$$

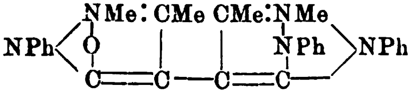
II.


$$\begin{matrix}\mathrm{NPh\cdot CCl} \\ \mathrm{N{=}CMe}\end{matrix}\!\!>\!\mathrm{C\cdot C}\!<\!\!\begin{matrix}\mathrm{CCl{-}NPh} \\ \mathrm{CMe{:}N}\end{matrix}$$

III.


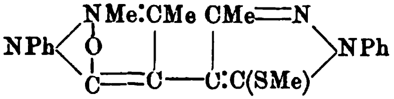
IV.


V.


VI.


Bis-5-chloro-1-phenyl-3-methylpyrazole, (II), yields with methyl iodide a *dimethiodide*, which is converted by potassium hydrogen sulphide, ammonia, or aniline into *bispyrines*.

The mixed and the bispyrines are well-characterised, crystalline substances. The anilopyrines melt at the lowest, the iminopyrines at the highest, temperatures. Antithiopyrine resembles antipyrine and thiopyrine; it forms a dihydrochloride, but combines with only 1 mol. of methyl iodide, which is attached to the thiopyrine half of the molecule. This *methiodide* loses methyl iodide when heated, forming *anti-ψ-thiopyrine*. Antianilopyrine yields a similar *anti-ψ-anilopyrine*.



5-Chloro-1 : 1′-diphenyl-3 : 3′-dimethyl-4′ : 5′-dihydrobispyrazole-5-one, $C_8N_2ClMePh \cdot C_8N_2HOMePh$, crystallises in white needles, m. p. 240°. The *methiodide*,

$$C_{22}H_{22}ON_4ClI,4H_2O,$$

crystallises in leaflets, m. p. 203°, loses part of the water of crystallisation in a vacuum over sulphuric acid and the remainder at 115°, and yields bisantipyrine when heated with alkalis in alcoholic solution. The product, obtained on heating the 5-chlorodihydrobispyrazole-5′-one with methyl iodide, crystallises in colourless leaflets, containing $4H_2O$, m. p. 209°, and is a mixture of antipyrinyl-5-iodopyrazole and antipyrinyl-5-chloropyrazole methiodides. The *methochloride* of antipyrinyl-5-chloropyrazole, $C_{22}H_{22}ON_4Cl_2$, crystallises in white needles, m. p. 213°, and forms two *platinichlorides*: $(C_{22}H_{22}ON_4Cl_2)_2PtCl_4$, yellow prisms, m. p. 236°, and $C_{22}H_{22}ON_4Cl_2,HCl,PtCl_4$, a yellow, crystalline mass, decomposing without melting at high temperatures.

Antithiopyrine, $C_{22}H_{22}ON_4S,2H_2O$, separates from water in monoclinic crystals, from ether in needles, m. p. 225°, and gives with sulphurous acid an intense yellow, or with ferric chloride a reddish-brown, coloration which gradually fades. The *hydrochloride*,

$$C_{22}H_{22}ON_4S,2HCl,$$

crystallises in deliquescent needles; the *platinichloride*,

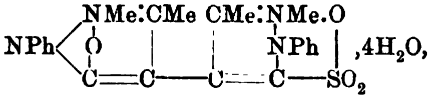
$$C_{22}H_{22}ON_4S,H_2PtCl_6,4H_2O,$$

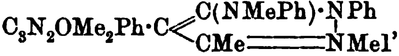
is obtained as a yellowish-red precipitate. The *methiodide*,

$$C_3N_2OMe_2Ph\cdot C_3N_2MePh(MeI)\cdot SMe,$$

formed by the action of methyl iodide on antithiopyrine, crystallises in needles, m. p. 192°, and forms a dark red, crystalline *dibromide*, $C_3N_2OMe_2Ph\cdot C_3N_2MePh(MeBr)\cdot SBr$, m. p. 189° (decomp.), when treated with bromine in chloroform solution.

Anti-ψ-thiopyrine (*5-methylthiol-1-phenyl-3-methyl-4-antipyrinylpyrazole*), formed by distilling antithiopyrine under reduced pressure, is obtained in colourless crystals, m. p. 168°. *Antithiopyrine trioxide* (annexed formula) is formed in stout crystals by the action of potassium sulphite on the methiodide, (III). It cannot be obtained by oxidation of antithiopyrine, as this leads to the formation of resins.

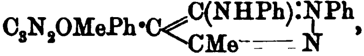


Antianilopyrine, $C_{28}H_{27}ON_5$, m. p. 215°, forms yellow crystals, probably isomorphous with bisantipyrine, absorbs carbon dioxide from the air, has a strong alkaline reaction to litmus, and gives a reddish-yellow coloration with alcoholic ferric chloride; when dissolved in acids and precipitated by addition of alkalis, it yields a white precipitate, which becomes yellow only gradually and may be the ammonium hydroxide. The *hydrochloride*, $C_{28}H_{27}ON_5,2HCl$, m. p. 106°, *platinichloride*, $C_{28}H_{27}ON_5,H_2PtCl_6,3H_2O$, *aurichloride*, m. p. 117°, *mercurichloride*, m. p. 157°, and *picrate*, m. p. 228°, are described. The *methiodide*,  $C_3N_2OMe_2Ph\cdot C<\begin{matrix}C(NMePh)\cdot NPh\\ \quad\quad\quad\quad\quad | \\ CMe{=\!=\!=}NMeI\end{matrix}$, formed by the action of methyl iodide on antianilopyrine at the ordinary temperature, could not be crystallised. The corresponding *methochloride* forms a *platinichloride*, $C_{28}H_{27}ON_5,MeCl,HCl,PtCl_4,2H_2O$, crystallising in yellow needles. The *benziodide*, $C_{28}H_{27}ON_5,CH_2PhI$, forms colourless crystals, m. p. 126°. The *additive* compound with acetyl iodide,

$$C_3N_2OMe_2Ph\cdot C_3N_2MePh(MeI)\cdot NPhAc,$$

crystallises in colourless prisms, m. p. 116°.

5-*Anilino*-1-*phenyl*-3-*methyl*-4-*antipyrinylpyrazole*,



$$C_3N_2OMePh\cdot C<\begin{matrix}C(NHPh):NPh\\ \quad\quad\quad\quad\quad | \\ CMe{=\!=\!=}N\end{matrix},$$

prepared by heating antianilopyrine hydrochloride, or a mixture of the base with ammonium chloride, or by the action of aniline at 180—200° on the mixed methiodide obtained from (I), crystallises in white leaflets, m. p. 240°, is neutral in alcoholic solution, and gives a yellow coloration with ferric chloride. The *platinichloride*,

$$(C_{27}H_{25}ON_5)_2,H_2PtCl_6,$$

forms yellowish-red crystals. When heated with methyl iodide at 100°, the base yields a *salt* from which antianilopyrine is obtained on treatment with sodium hydroxide.

Anti-ψ-anilopyrine (5-*methylanilino*-1-*phenyl*-3-*methyl*-4-*antipyrinylpyrazole*, $C_3N_2OMe_2Ph\cdot C_3N_2MePh\cdot NMePh$, prepared by heating antianilopyrine methiodide, forms colourless crystals, m. p. 101°; the *platinichloride*, $(C_{28}H_{27}ON_5)_2,H_2PtCl_6,4H_2O$, crystallises in small, yellowish-red needles.

5-*Acetylanilino*-1-*phenyl*-3-*methyl*-4-*antipyrinylpyrazole*,

$$C_3N_2OMe_2Ph\cdot C_3N_2MePh\cdot NPhAc,$$

formed by heating the *additive* compound of acetyl iodide and antianilopyrine, crystallises in white leaflets, m. p. 238°.

Anti-iminopyrine crystallises in white leaflets, m. p. 259—260° (decomp.), and is a strong base. The *platinichloride*,

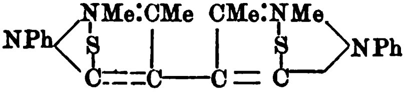
$$C_{22}H_{23}ON_5,H_2PtCl_6,H_2O,$$

forms yellowish-red prisms. The *methiodide*, and *anti-ψ-iminopyrine*, obtained from it by heating, are oils. 5-*Amino*-1-*phenyl*-3-*methyl*-4-*antipyrinylpyrazole*, $C_3N_2OMe_2Ph\cdot C_3N_2MePh\cdot NH_2$, formed by heating the methiodide, (III), with ammonia at 250°, crystallises in white needles, m. p. 220°, and is neutral in aqueous or alcoholic solution. The *acetyl* derivative, $C_{23}H_{28}O_2N_5$, crystallises in colourless needles, m. p. 237°.

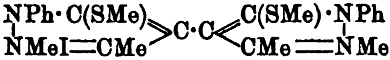
Bis-5-*chloro*-1-*phenyl*-3-*methylpyrazole*, $C_{20}H_{16}N_4Cl_2$, crystallises in white needles, m. p. 160°, and is soluble in concentrated hydrochloric acid. The *dimethiodide*, $C_{22}H_{22}N_4Cl_2I_2,3H_2O$, crystallises in leaflets, m. p. 205°, and loses $2H_2O$ in a vacuum. When heated with methyl iodide, bischlorophenylmethylpyrazole yields a *product*, m. p. 210—215° (decomp.), consisting chiefly of bis-5-iodo-1-phenyl-3-methylpyrazole methiodide. The *methochloride* (*bisantipyrine chloride*),

$$C_{22}H_{22}N_4Cl_4,H_2O,$$

m. p. 225°.

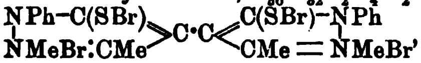


Bisthiopyrine forms white crystals, m. p. 237°, is soluble in hydrochloric acid, and gives with ferric chloride a yellow coloration or with sulphurous acid a yellow, crystalline *precipitate*; the *platinichloride*, $C_{22}H_{22}N_4S_2,H_2PtCl_6,4H_2O$, was analysed. The *dimethiodide*,



$$\begin{array}{l}NPh\cdot C(SMe)\\ NMeI{=}CMe\end{array}\!\!>C\cdot C<\!\!\begin{array}{l}C(SMe)\cdot NPh\\ CMe{=}NMeI\end{array},$$

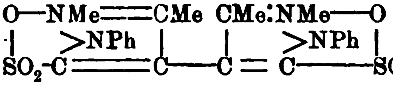
separates from water in crystals containing $2H_2O$, m. p. 154°, or from alcohol in anhydrous, white prisms, m. p. 234°. The similarly constituted *additive* product with benzoyl chloride, $C_{36}H_{32}O_2N_4Cl_2S_2$, m. p. 134°. The *tetrabromide*,



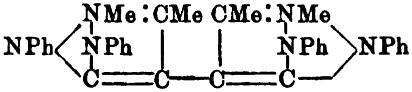
$$\begin{array}{l}NPh-C(SBr)\\ NMeBr{:}CMe\end{array}\!\!>C\cdot C<\!\!\begin{array}{l}C(SBr)-NPh\\ CMe{=}NMeBr\end{array},$$

forms a red, crystalline mass,

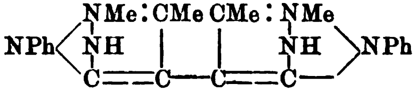
m. p. about 133°; the *tetrachloride* is deliquescent. *Bisthiopyrine trioxide*, formed by the action of chlorine on bisthiopyrine in aqueous or acetic acid solution, separates in stout crystals, and decomposes at high temperatures. *Bis-ψ-thiopyrine*, $SMe·C_3N_2MePh·C_3N_2MePh·SMe$, formed by heating bisthiopyrine methiodide at 200° under reduced pressure, distils as a viscid oil, and separates from alcohol in colourless crystals, m. p. 124°; it is oxidised by potassium permanganate in acetic acid solution, forming the *sulphone*, $C_{22}H_{22}O_4N_4S_2$, crystallising in white leaflets, m. p. 149°.



Bisanilopyrine crystallises in slightly yellow needles, m. p. 207°, and is a strong base. The *platinichloride*, $C_{34}H_{32}N_6,H_2PtCl_6,4H_2O$, *aurichloride*, $C_{34}H_{32}N_6,2HAuCl_4$, m. p. 218°, *hydriodide*, $C_{34}H_{32}N_6,2HI$, m. p. 328°, and *picrate*, m. p. 214°, are described. The *methiodide*, $C_{36}H_{38}N_6I_2,2H_2O$, forms colourless crystals, m. p. 120° (decomp.). *Bis-ψ-anilopyrine*, $NMePh·C_3N_2MePh·C_3N_2MePh·NMePh$, forms white crystals, m. p. 108°, and has a neutral reaction in alcoholic solution, but dissolves in acids. *Bis-5-anilino-1-phenyl-3-methylpyrazole*, $NHPh·C_3N_2MePh·C_3N_2MePh·NHPh$, prepared by heating bisanilopyrine hydrochloride or hydriodide, or by the action of aniline on bis-5-chloro-1-phenyl-3-methylpyrazole at 180—200°, crystallises in white needles, m. p. 315°, and is converted into bisanilopyrine hydriodide when heated with methyl iodide.



Bisiminopyrine crystallises in white leaflets, m. p. 250° (decomp.), has strong basic properties, and forms an oily *methiodide*. The *hydriodide*, $C_{22}H_{24}N_6,2HI$, forms white crystals, m. p. 280°; the *picrate*, $C_{22}H_{24}N_6,C_6H_3O_7N_3$, forms golden leaflets, m. p. 204°. The *dibenzenesulphonyl* compound, $C_{22}H_{22}N_6(SO_2Ph)_2$, m. p. 198°. The crystalline *platinichloride*, $C_{22}H_{24}N_6,H_2PtCl_6$, is yellowish-red. *Bis-5-amino-1-phenyl-3-methylpyrazole*, $NH_2·C_3N_2MePh·C_3N_2MePh·NH_2$, formed by heating bisantipyrine chloride with ammonia at 250°, yieldsa *diacetyl* derivative crystallising in colourless needles, m. p. 272°. G. Y.



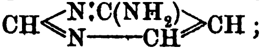
Diazoamino-compounds Derived from Purine Bases. RICHARD BURIAN (*Zeitsch. physiol. Chem.*, 1907, 51, 425—437. Compare Abstr., 1904, i, 354).—A good yield of the diazobenzenesulphonyl derivative of adenine can be obtained only in the absence of an excess of alkali. The compound when prepared is also readily decomposed by alkalis. Full details for the preparation are given. It forms pale yellow, microscopic needles which decompose at 200° without melting. It is partially decomposed when boiled with water.

Guanine, xanthine, and theophylline react with diazobenzenesulphonic acid even in the presence of an excess of alkali. Purine bases in which a methyl group is in the position 7, for example, caffeine and theobromine, do not react either in the presence or absence of excess of alkali.

Nucleic acids, although they contain guanine and adenine residues, do not condense with the diazosulphonic acid in the presence or absence of excess of alkali. The conclusion is drawn that guanine or adenine is attached at position 7 to the residue of the nucleic acid molecule and also that this union is effected by means of phosphorus.

J. J. S.

Pyrimidine Derivatives from Purine Bases. RICHARD BURIAN (*Zeitsch. physiol. Chem.*, 1907, 51, 438—456).—In order to determine whether some of the pyrimidine derivatives obtained by hydrolysing nucleic acids with moderately concentrated sulphuric acid may not be formed from purine bases by hydrolysis and reduction, experiments have been made by heating adenine and guanine with 30—40% sulphuric acid and dextrose or any other carbohydrate as a reducing agent. The results show that pyrimidine derivatives are produced under these conditions. From adenine, a product has been isolated which corresponds in composition with 6-*aminopyrimidine*,



$$CH{<}\begin{matrix}N{:}C(NH_2)\\ N\text{——}CH\end{matrix}{>}CH\,;$$

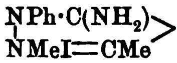
it yields a *picrate*, $C_4H_5N_3,C_6H_3O_7N_3$, which crystallises in pale yellow needles, softens at 215°, m. p. 235—240° (decomp.). The *platinichloride*, $(C_4H_5N_3)_2,H_2PtCl_6$, crystallises in glistening, yellow prisms. A second product is 6-hydroxypyrimidine.

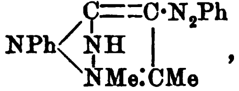
From guanine, Wheeler and Johnson's *iso*cytosine or 2-amino-6-oxypyrimidine (Abstr., 1903, i, 526) has been obtained together with uracil, which is produced by the removal of the amino-group from the *iso*cytosine.

From 2 grams of guanine, 1·56 were recovered unaltered, and 0·234 gram was accounted for as *iso*cytosine.

The results obtained account for the fact that in the estimation of purine bases a dilute sulphuric acid (½ to 1%) should be used.

J. J. S.

5-Alkylamino-1-phenyl-3-methylpyrazole-4-azobenzene and 4:5-Diamino-1-phenyl-3-methylpyrazole. AUGUST MICHAELIS and HANS KLOPSTOCK (*Annalen*, 1907, 354, 102—115).—It was shown previously that the chlorine atom of 5-chloro-1-phenyl-3-methylpyrazole-4-azobenzene is substituted readily by hydrogen, iodine, or the group SH (Michaelis, Abstr., 1905, i, 392). It is found now that whilst primary and secondary aliphatic amines, as also piperidine, react easily with this chloropyrazole, ammonia is almost without action even at high temperatures. On the other hand, the corresponding iodopyrazole reacts with alcoholic ammonia at 200—210°, forming 5-amino-1-phenyl-3-methylpyrazole-4-azobenzene (Michaelis and Danzfuss, Abstr., 1905, i, 476). With methyl iodide, this 5-amino-pyrazole forms a *methiodide*,  $\left.\begin{array}{l}NPh\cdot C(NH_2)\\ NMeI{=}CMe\end{array}\right>C\cdot N{:}NPh$, which may be regarded as the hydriodide of *iminopyrine-4-azobenzene*,



into which it is easily converted.

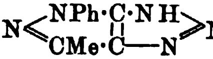
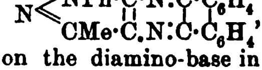
5-*Amino*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene platinichloride*, $(C_{16}H_{15}N_5)_2H_2PtCl_6$, forms a yellowish-red, sparingly soluble precipitate decomposing at 199°. The *methiodide* crystallises in scales, m. p. 225°; the *methochloride* forms yellow leaflets, m. p. 126°, and when treated with aqueous potassium hydroxide yields *iminopyrine*-4-*azobenzene*; this crystallises in yellowish-red leaflets, m. p. 161°, and has strong basic properties. The *platinichloride*, $(C_{17}H_{17}N_5)_2,H_2PtCl_6$, forms red needles, m. p. 225°; the *mercurichloride*, $C_{17}H_{17}N_5,HCl,HgCl_2$, m. p. 201°.

5-*Ethylamino*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene*, $C_{18}H_{19}N_5$, forms yellowish-red crystals, m. p. 51°; the *hydrochloride*, $C_{18}H_{19}N_5,HCl$, crystallises in red needles, m. p. 99°; the *platinichloride*, yellowish-red crystals, m. p. 184°; the *methiodide*, yellow scales, m. p. 218°. *Ethyliminopyrine*-4-*azobenzene*, formed from the preceding methiodide, yields a *platinichloride*, $(C_{19}H_{22}N_5Cl)_2PtCl_4$, m. p. 212°.

5-*Diethylamino*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene*, $C_{20}H_{23}N_5$, forms yellowish-red crystals, m. p. 82°.

5-*Piperidyl*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene*, $N_2Ph\cdot C_3N_2MePh\cdot C_5NH_{10}$, crystallises in yellowish-red needles, m. p. 112°; the *hydrochloride*, $C_{21}H_{23}N_5,HCl$, red powder, m. p. 142°; the *methiodide*, yellow needles.

4 : 5-*Diamino*-1-*phenyl*-3-*methylpyrazole*, $C_3N_2MePh(NH_2)_2$, prepared by reduction with stannous chloride and hydrochloric acid of 5-amino-1-phenyl-3-methylpyrazole-4-azobenzene or the 4-*azobenzenesulphonic acid*, $C_{16}H_{15}O_3N_5S$, m. p. 255°, or 4-*iso*nitroso-5-imino-1-phenyl-3-methylpyrazolone (Walther, Abstr., 1897, i, 297), crystallises in needles, m. p. 119°, and reduces Fehling's and ammoniacal silver solutions in the cold; the *hydrochloride*, $C_{10}H_{12}N_4,2HCl$, is more stable than the base on exposure to air.

1-*Phenyl*-3-*methyl*-4 : 5-*aziminopyrazole*,  $N\left<\begin{array}{l}NPh\cdot C\cdot NH\\ CMe\cdot C{-}N\end{array}\right>N$, formed by the action of sodium nitrite on the diamino-base in acetic acid solution at 0°, crystallises in slightly yellow needles, m. p. 190° (decomp.). The *phenanthrazine* derivative,  $N\left<\begin{array}{l}NPh\cdot C\cdot N{:}C\cdot C_6H_4\\ CMe\cdot C.N{:}C\cdot C_6H_4\end{array}\right.$, prepared by the action of phenanthraquinone on the diamino-base in glacial acetic acid solution, crystallises in yellow needles, m. p. 265°, and forms a red solution in concentrated hydrochloric acid. 4 : 5-*Diacetylamino*-1-*phenyl*-3-*methylpyrazole*, $C_3N_2MePh(NHAc)_2$, m. p. 233°, is soluble in concentrated hydrochloric acid.

4-*Amino-5-piperidyl*-1-*phenyl-3-methylpyrazole*,

$$NH_2\cdot C_3N_2MePh\cdot C_5NH_{10},$$

prepared by reduction of 5-piperidyl-1-phenyl-3-methylpyrazole-4-azobenzene with stannous chloride and hydrochloric acid, forms colourless crystals, m. p. 87°, and reduces Fehling's or slightly acid platinum tetrachloride solutions. The salts do not crystallise readily. The *acetyl* derivative, $NHAc\cdot C_3N_2MePh\cdot C_5NH_{10}$, crystallises in white needles, m. p. 171°, and is soluble in dilute acids; the *benzoyl* derivative, $C_{22}H_{24}ON_4$, forms white crystals, m. p. 208°. G. Y.

Constitution of the Indole Group in Albumin. IV. Synthesis of Racemic Tryptophan. Alexander Ellinger and Claude Flamand (*Ber.*, 1907, 40, 3029—3033. Compare Abstr., 1904, i, 639; 1905, i, 827; 1906, i, 696).—The azlactone, obtained from oxidising tryptophan or from indole-3-aldehyde (*loc. cit.*), crystallises with 1 mol. chloroform in glistening, dark orange prisms, m. p. 220°. When heated with excess of 1% sodium hydroxide, the lactone ring opens, and acidification of the solution precipitates *a-benzoylaminoindolylacrylic acid*, $C_8H_6N\cdot CH:C(NHBz)\cdot CO_2H$, which crystallises from alcohol in glistening prisms, m. p. 232—234° (not sharp). Racemic tryptophan was prepared by reduction of the acrylic acid with sodium and alcohol, and the benzoyl group is hydrolysed on the addition of water. This substance behaves like the tryptophan, obtained from casein, towards naphthylcarbimide, naphthalene, and benzenesulphonyl chloride, and has the same m. p. and crystalline form. It is sweet, whereas the digestive tryptophan is almost tasteless, resembling racemic and *l*-leucine (compare E. Fischer, Abstr., 1906, i, 72). W. R.

Formation of Polypeptides by the Hydrolysis of Proteins. Emil Fischer and Emil Abderhalden (*Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 30, 574—590. Compare Abstr., 1906, i, 718).—Glycyl-*d*-alanine has been isolated from the products of the hydrolysis of silk-fibroin with hydrochloric acid; it is most readily obtained in the form of its β-naphthalenesulphonyl derivative,

$$C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$$

(Fischer and Bergell, Abstr., 1903, i, 24), m. p. 155° (corr.), which on hydrolysis yields β-naphthylsulphonylglycine and alanine.

A *tetrapeptide*, $C_{16}H_{22}O_6N_4$, has also been isolated from the hydrolytic products precipitated by phosphotungstic acid. This contains two glycine, one alanine, and one tyrosine residues; it has not been obtained in a crystalline form, dissolves readily in water, but is insoluble in absolute alcohol. It is not precipitated by the addition of concentrated sodium chloride solution except in the presence of a little nitric or acetic acid. When completely hydrolysed by boiling with 25% sulphuric acid, the products are glycine, alanine, and tyrosine. When partially hydrolysed with concentrated hydrochloric acid at 16°, glycyl-*d*-alanine anhydride and glycyl-*l*-tyrosine anhydride are formed.

Elastin with 70% sulphuric acid at 36° yields *d*-alanyl-*l*-leucine, and with fuming hydrochloric acid at the same temperature, *l*-leucylglycyl anhydride and *l*-leucyl-*d*-alanine anhydride. These anhydrides do not crystallise so readily as the specimens prepared synthetically, and the possibility of isomerism is suggested.

The compounds crystallise readily after their aqueous solutions have been repeatedly evaporated, after boiling with quinoline, or after sublimation. Other compounds isolated from the hydrolytic products of elastin are a gelatinous *alanylproline anhydride*, $C_8H_{12}O_2N_2,H_2O$, and glycylvaline anhydride, $C_7H_{12}O_2N_2$, m. p. 245—250° (corr.).

The partial hydrolysis of diglycylglycine and of pentaglycylglycine has been studied. J. J. S.

Amount of Oxygen in Horses' Oxyhæmoglobin. M. Piettre and Antony Vila (*Compt. rend.*, 1907, **144**, 1370—1372).—Crystals of oxyhæmoglobin contained 0·80 c.c. to 0·95 c.c. of oxygen per gram of dry matter. When dissolved in pure water, the substance gives up a much greater amount (1·4 c.c. to 1·7 c.c.).

The spectrum of solutions of oxyhæmoglobin reduced by the action of a vacuum and heat (45—50°) includes the bands $\lambda = 634$. The union of bands α and β did not take place. N. H. J. M.

Action of Hydrogen Peroxide on Hæmin. John A. Gardner and G. A. Buckmaster (*Proc. physiol. Soc.*, 1907, xxxii—xxxiv.; *J. Physiol.*, **35**).—When purified hæmin crystals are treated with dilute hydrogen peroxide, oxygen is evolved, and the solution shows traces of ferric chloride and free hydrochloric acid. With concentrated hydrogen peroxide, the crystals are eroded, and the chief products formed are carbon dioxide and oxalic acid; the chlorine and iron are all liberated, and about two thirds of the nitrogen is combined in the form of ammonium salts. Complex organic acids to the amount of 2—4% of the hæmin taken were also formed. These hæmatic acids were evidently identical with the oxidation products obtained by Kuster by other methods. W. D. H.

Colouring Matter of Blood. VII. Leo Marchlewski and St. Mostowski (*Zeitsch. physiol. Chem.*, 1907, **51**, 464—467. Compare Abstr., 1904, i, 463, 839; 1905, i, 399, 725; 1906, i, 779. Compare Kütscher, *Annalen*, 1906, **346**, 9).—From the behaviour of hæmopyrrole towards sulphuric acid and diazobenzene chloride, the authors come to the conclusion that the base is chemically acted on by the sulphuric acid, probably polymerised. The base itself is probably homogeneous. The acid solution, obtained by shaking the ethereal solution of hæmopyrrole with sulphuric acid, yields, when neutralised with sodium carbonate, a product which also condenses with diazobenzene chloride. J. J. S.

Nucleic Acids. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1907, **51**, 549).—Polemical against Burian. W. D. H.

Nucleic Acids. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1907, **52**, 62).—By the oxidation of nucleic acid with nitric acid, the barium salt of a new acid, $C_6H_{10}O_8$, was obtained. This originates from the carbohydrate group of the nucleic acid, and it is termed without prejudice, *episaccharic acid.* Its *quinine* salt, $C_{20}H_{24}O_2N_2,C_6H_{10}O_8,2H_2O$, crystallises in long needles which are sparingly soluble in water.

W. D. H.

Relation of Collagen and Gelatin. A. D. Emmett and William J. Gies (*Proc. Amer. physiol. Soc.*, 1907, xi; *Amer. J. Physiol.*, **19**).—If gelatin is continuously dried at 130° it is not, as Hofmeister stated, converted into collagen. The dried product is somewhat less soluble than the original gelatin, but it is digested by trypsin with equal readiness, whereas collagen is not affected. That gelatin is not a simple hydrate of collagen is shown by the fact that ammonia is liberated from collagen when the latter is converted into gelatin by boiling with water. W. D. H.

Action of Nitrous Acid on Gelatin. John Seemann (*Zeitsch. Biol.*, 1907, **49**, 494—502).—Nitrous acid is a suitable reagent for studying the constitution of proteins; it acts as a deamidising reagent, and so part of the yield consists of hydroxy-acids free from the amino-group, and another part consists of the amino-acids in peptide linking. In the present research with gelatin, among other substances, hydrogen cyanide was obtained; this is regarded as probably derived from an intermediate nitroso-derivative of the guanidine residue of arginine. If leucine or asparagine are treated in the same way, no hydrogen cyanide was obtained, but guanidine carbonate and especially creatinine yielded it. From the deamidised portion, pure sulphur was crystallised out (1 gram from 1250 grams of gelatin). The ethereal extract contained no pyrotartaric acid, but oxalic acid was present; the old formula for cystein therefore probably needs revision, and the origin of the sulphur is obscure. The only volatile fatty acids which were identified are lactic and acetic, but others are present. W. D. H.

Deaminoglutin. II. Zdenko H. Skraup (*Monatsh.*, 1907, **28**, 447—459).—The hydrolysis of deaminoglutin has been repeated on a large scale and the results previously obtained (Abstr., 1906, i, 913) confirmed. In addition to glycine, histidine, and arginine, leucine, proline and alanine have been obtained by the hydrolysis of deaminoglutin, but not lysine. This latter compound is, however, present in the products produced by the hydrolysis of glutin, so that it is evident that lysine occupies an exposed position in the glutin molecule. The picrate, m. p. 153—155°, which is obtained from deaminoglutin in place of the lysine, is probably a mixture, since, on treatment with dilute sulphuric acid, there is obtained from it a compound, m. p. 254°, which is probably an aminohydroxyvaleric acid, $C_5H_{11}O_3N$, and another substance, m. p. 217—218°. From the analytical results, this substance is either an aminovaleric acid, $C_5H_{11}O_2N$, or an anhydride of aminohydroxyvaleric acid, $C_5H_9O_2N$, but the former is more probable, since it yields a well-defined, crystalline copper salt. These acids are not derived from the arginine, since the latter compound is obtained both from deaminoglutin and glutin to about the same extent, so that it is probable that besides the arginine residue, there is present in glutin a diaminovaleric acid. W. H. G.

Thioglutin. Wl. S. Sadikoff (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 411—422).—When collagen is heated with alkalis, the general properties of the gummy complex seem to be destroyed, but when an aqueous solution of glutin is heated with alkalis, in the presence of carbon disulphide, a sulphur derivative, *thioglutin*, is formed, which very readily undergoes both condensation and hydrolysis. It is combined with water in a colloidal state, which, when removed, causes the thioglutin to decompose. Thioglutin consists chiefly of a gelatinous substance combined with a base, such as sodium, calcium, &c., the calcium compound being the most gelatinous and stable. Thioglutin contains 3% to 4% of sulphur and 3·6% to 7·6% of calcium; it forms definite, unstable, very gelatinous *salts* with lead and tannin. A hot solution of thioglutin forms a gelatinous mass on cooling, which on gradual desiccation at the ordinary temperature, whether exposed to the atmosphere or not, becomes covered with a bright red crust, a condensation product not containing any gummy complex. In the presence of water, the colour is deepened, whilst different salts produce various shades of colour in this crust. On precipitation with alcohol and drying, thioglutin is converted into *thioglutan*, which itself readily decomposes, forming a soluble and an insoluble substance. By treating collagen with calcium sulphide, sulphur derivatives are obtained very similar to thioglutin, but not so strongly gelatinous. Z. K.

Behaviour of Opsonin and Serum Proteins During Pressure Filtration. Warrington Yorke (*Bio-Chem. J.*, 1907, **2**, 357—362).—Serum was filtered under pressure through a Pasteur-Chamberland filter; as filtration proceeded, less and less and finally no protein came through. Opsonins do not pass a filter of this kind and are non-dialysable through parchment paper. These facts, together with Tamar and Bispham's observation (*J. Exper. Med.*, Dec., 1906) that they are precipitable with euglobulin by half saturation with ammonium sulphate, are in favour of the protein-like nature of opsonins.
W. D. H.

Atoxyl. Ernest Fourneau (*J. Pharm. Chim.*, 1907, [vi], **25**, 528—537).—Since the publication of the author's preliminary note on the subject (*ibid.*, 32), Ehrlich and Bertheim have suggested that atoxyl has the constitution $NH_2\cdot C_6H_4\cdot AsO(OH)\cdot ONa,4H_2O$ (*Berl. klin. Woch.*, 1907, 682). The author has now compared the substance with the so-called arsenanilide, prepared by Béchamp in 1863, and finds that the two are identical. Atoxyl crystallises with $5H_2O$ and loses $3H_2O$ by efflorescence. The anhydrous substance is readily soluble in methyl alcohol. The reactions of its aqueous solution with solutions of various metallic salts and a detailed account of its therapeutic action are given in the original. T. A. H.

Organic Chemistry.

Equilibrium Isomerism on Heating Bromides of the Compositions $C_nH_{2n+1}Br$ and $C_nH_{2n}Br_2$. Alexei Fawobsky (*Annalen*, 1907, **354**, 325—389. Compare Abstr., 1895, i, 496; Ageewa, Abstr., 1905, i, 776).—Reversible, intramolecular transformations of isomerides, which take place under the influence of a catalyst such as potassium hydroxide, may be represented by the equation $A + K \rightleftharpoons A' + K$, in which A and A′ are the isomerides and K is the catalyst. Consideration of the mechanism of these reactions led to the expectation that such transformations taking place in the absence of a catalyst would be found also to be reversible. Such cases have been found in the intramolecular transformations of the bromides $C_nH_{2n+1}Br$ and $C_nH_{2n}Br_2$, which take place when these are heated.

According to Aronstein (Abstr., 1881, 567), *n*-propyl bromide dissociates at 280° into propylene and hydrogen bromide, which recombine, forming *iso*propyl bromide. It is found now that on five successive heatings for eight hours at 250°, the fraction, b. p. 69—70°, being removed after each heating, 200 grams of *iso*propyl bromide yield 40 grams of *n*-propyl bromide. Hence the transformation is reversible, as expressed by the equation $CH_2Me\cdot CH_2Br = CHMe{:}CH_2 + HBr = CHMe_2Br$, and the addition of hydrogen bromide to propylene must take place in part contrary to Markownikoff's rule.

Similar, but more complicated, results are obtained with other bromides and dibromides. The discussion of the results leads to the conclusion that tautomerism and the reversible, intramolecular transformations of ordinary isomerides are analogous phenomena and may be included in one group, to which Schaum's term, equilibrium isomerism, is applied.

I. *Equilibrium Isomerism on heating* iso*Butyl and* tert.-*Butyl Bromides.*—[With Wad. Tolstopjatoff.]—Eltekoff found (*Ber.*, 1875, 8, 1244) that the transformation of *iso*butyl into *tert.*-butyl bromide, which takes place slowly at 145°, more rapidly at higher temperatures, reaches an equilibrium independently of the temperature when 20% of the *iso*bromide remains unchanged, but later (*Inaug. Diss.*, *Charkoff*, 1884) considered that the transformation probably takes place completely. The experiments described in this paper show that the transformation is reversible, and that an equilibrium between the two isomerides is established when either bromide is heated at 210—220°; the main reaction is represented by the equilibrium equation: $CMe_3Br \rightleftharpoons CMe_2{:}CH_2 + HBr \rightleftharpoons CHMe_2\cdot CH_2Br$. Part of the intermediately formed *iso*butylene reacts with *iso*butyl bromide, $CMe_2{:}CH_2 + CMe_3Br = CMe_2\cdot CH_2\cdot CMe_2Br$, forming *iso*dibutyl bromide.

II. *Equilibrium Isomerism on heating Bromo*iso*pentanes.*—[With E. Fritzmann.]—Eltekoff (*loc. cit.*) found that *iso*amyl bromide is transformed at 256—260° into the *tert.*-bromide, which is found now to yield, at 220°, 15—20% of the *sec.*-bromide, 3—4% of the two primary amyl bromides, and 1—2% of higher brominated by-products, 75—80% remaining unchanged. The equilibrium is represented by the equation $CH_2Br\cdot CH_2Pr^{\beta} \rightleftharpoons CH_2{:}CHPr^{\beta} + HBr \rightleftharpoons CHBrMePr^{\beta} \rightleftharpoons CHMe{:}CMe_2 + HBr \rightleftharpoons CBrMe_2Et \rightleftharpoons CH_2{:}CMeEt + HBr \rightleftharpoons CH_2Br\cdot CHMeEt$.

The reactions take place in part, not only contrary to Markownikoff's, but also to Saytzeff's, rule that on formation of a hydrogen haloid from an alkyl haloid the hydrogen atom is split off from the less hydrogenated carbon atom.

III. *Equilibrium Isomerism on heating Ethylene and Ethylidene Dibromides.*—[With N. SOKOWNIN and ŽINEWSKY.]—The equilibrium mixture of ethylene and ethylidene dibromides, obtained on heating either isomeride, contains chiefly ethylene dibromide. Thus 40 grams of ethylene dibromide, b. p. 130—131°, when heated at 300—315°, yields 3·5 grams, b. p. 106·5—110·5°; ethylidene dibromide has b. p. 108°. Ethyl bromide and tribromoethane, formed according to the equations $C_2H_4Br_2 + HBr \rightleftharpoons C_2H_5Br + Br_2$ and $C_2H_4Br_2 + Br_2 \rightleftharpoons C_2H_3Br_3 + HBr$, are found as by-products. The ethylidene dibromide, formed from its isomeride, is identified by conversion into the *dibenzoate*, $CHMe(OBz)_2$, which crystallises in colourless prisms, m. p. 72°. A mixture of this with ethylene dibenzoate, m. p. 71·5°, formed from ethylene dibromide, had m. p. 51°.

IV. *Equilibrium Isomerism on heating Dibromopropanes.*—[With N. SOKOWNIN.]—Propylene dibromide remains almost unchanged at 200—205°, but at 240—250° is transformed to the extent of 2—3% into trimethylene dibromide. This, on the other hand, when heated at 240—250°, yields an equilibrium mixture consisting chiefly of propylene dibromide together with trimethylene dibromide, *n*- and *iso*-propyl bromides, and tribromopropane, whilst dibromoacetol at 220—230° is transformed almost entirely into propylene dibromide together with only traces of trimethylene dibromide. Small amounts of dibromoacetol, formed when propylene dibromide is heated at 225—230°, are identified by conversion into the dibenzoate. The presence of the unknown propylidene dibromide in these equilibrium mixtures could not be determined.

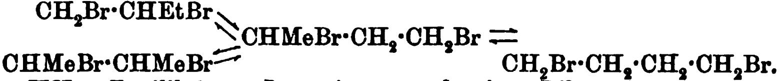
V. *Equilibrium Isomerism on heating Dibromo*iso*butanes.*—[With N. SOKOWNIN.]—When heated at 205—220°, *iso*butylene dibromide yields chiefly β-methyltrimethylene dibromide together with small amounts of *iso*- and *tert.*-butyl bromides and tribromo*iso*butane.

β-Methyltrimethylene dibromide, $CHMe(CH_2Br)_2$, b. p. 177·5—178°/765 mm., D_0^0 1·8515, D_0^{20} 1·8207, is reduced by zinc dust and alcohol at 60—93°, forming methyl*cyclo*propane together with traces of *iso*butylene, and when heated with silver acetate forms a *diacetate*, b. p. 211—214°/770 mm., which, on hydrolysis, yields β-methyltrimethylene glycol, $C_4H_{10}O_2$, b. p. 110—111°/14·5 mm. or 214—214·5°/771 mm., D_0^0 1·0297. This, on oxidation with potassium permanganate, forms methylmalonic acid.

When heated at 210—225°, β-methyltrimethylene dibromide is transformed to the extent of more than 50% into *iso*butylene dibromide. The presence of *iso*butylidene dibromide in the equilibrium mixtures has not been established; in any case, it would be present only in traces.

VI. *Equilibrium Isomerism on heating Dibromo-*n*-butanes.*—[With N. Sokownin.]—When heated at 215—220°, 114 grams of αβ-dibromo-*n*-butane, b. p. 99—99·5°/100 mm. or 165—166°/760 mm., yields 6·5 grams of a fraction, b. p. 59—62·5°/25 mm. or 158—161°/759 mm., which consists, at least for the most part, of βγ-dibromo-*n*-butane, as on successive treatment with sodium ethoxide and bromine it forms ββγγ-tetrabromobutane.

When heated at 220—230°, 280 grams of βγ-dibromo-*n*-butane, containing small amounts of the αβ-isomeride formed from *iso*butyl alcohol (Abstr., 1890, 1218), yields 40 grams of αγ-dibromo-*n*-butane, b. p. 173·5—176·5°/767 mm. (Demjanoff, Abstr., 1895, i, 161), and 10 grams of αδ-dibromo-*n*-butane (Hamonet, Abstr., 1905, i, 403). Omitting the intermediately formed hydrogen bromide and isomeric butylenes, the equilibrium is represented by the equation :

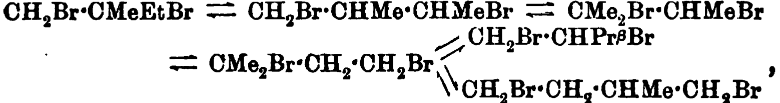


$$\left.\begin{array}{l}CH_2Br\cdot CHEtBr\\ CHMeBr\cdot CHMeBr\end{array}\right\rangle CHMeBr\cdot CH_2\cdot CH_2Br \rightleftharpoons CH_2Br\cdot CH_2\cdot CH_2\cdot CH_2Br.$$

VII. *Equilibrium Isomerism on heating Dibromoisopentanes.*—[With L. Kutscheroff.]—After being heated at 180—185°, 1850 grams of β-methyl-Δ^β-butylene dibromide, b. p. 47·5—48°/10 mm. (Ipatieff, Abstr., 1896, i, 401), yields three fractions. The fraction, b. p. 61—65°/10 mm., 550 grams, contains βδ-dibromo-β-methyl-*n*-butane, which, on hydrolysis with potassium carbonate, yields αα-dimethyltrimethylene glycol (Kondakoff, Abstr., 1893, i, 541) together with traces of *iso*propylethylene dibromide. The fraction, b. p. 68—70°/10 mm., 115 grams, contains βδ-dibromo-β-methyl-*n*-butane together with smaller amounts of *iso*propylethylene and β-methyltetramethylene dibromides. The fraction, b. p. 80—83°/11·5 mm., 44 grams, contains *β-methyltetramethylene dibromide*, $CH_2Br\cdot CHMe\cdot CH_2\cdot CH_2Br$, D_0^0 1·7491, D_0^{20} 1·7225, which forms a *diacetate*, $C_5H_{10}(OAc)_2$, b. p. 113°/12 mm. This, on hydrolysis, forms *β-methyltetramethylene glycol*, $C_5H_{12}O_2$, b. p. 131—133°/18 mm., which, on oxidation with potassium permanganate, yields methylsuccinic acid. Ethyltrimethylene dibromide is not present.

The equilibrium mixture, obtained by heating βδ-dibromo-β-methyl-*n*-butane at 180—185°, contains chiefly trimethylethylene dibromide and small amounts of *αβ-dibromo-β-methyl-*n*-butane*, $CH_2Br\cdot CMeEtBr$, b. p. 63—65°/18 mm. ; when heated with water and lead dioxide, distilled, and treated with moist silver oxide, this yields methyl *iso*propyl ketone and silver *iso*valerate, $C_5H_9O_2Ag$, which must be derived from αα-methylethylethylene.

Of the substances represented in the equilibrium equation :



$$CH_2Br\cdot CMeEtBr \rightleftharpoons CH_2Br\cdot CHMe\cdot CHMeBr \rightleftharpoons CMe_2Br\cdot CHMeBr \rightleftharpoons CMe_2Br\cdot CH_2\cdot CH_2Br \left\langle\begin{array}{l}CH_2Br\cdot CHPr^\beta Br\\ CH_2Br\cdot CH_2\cdot CHMe\cdot CH_2Br\end{array}\right. ,$$

only αγ-dibromo-β-methyl-*n*-butane has not been isolated.

Primary and secondary monobromo- and tribromo-*iso*pentanes are shown to be present in the fractions, having the lowest boiling points, obtained from the equilibrium mixture formed by heating β-methyl-Δ^{β}-butylene dibromide. G. Y.

Chloromethylnitrolic Acid. GIACOMO PONZIO (*Atti R. Accad. Sci. Torino*, 1907, **42**, 780—788).—It was stated by Glutz (*J. pr. Chem.*, 1870, 1, 141) and by Barbaglia (this Journ., 1873, 877) that the action of concentrated nitric acid on chloroacetone yields a compound, $C_3H_4O_2NCl$, which was afterwards shown to be chloro*iso*nitrosoacetone. But Tcherniac (Abstr., 1892, 1425) demonstrated that the compound used by Barbaglia and probably also by Glutz was not chloroacetone, but a mixture of dichloroacetone and acetone. The author finds that the interaction of true chloroacetone and concentrated nitric acid yields chloromethylnitrolic and oxalic acids. The reaction proceeds with intermediate formation of chloro*iso*nitrosoacetone, thus:

$$CH_2Cl\cdot COMe \longrightarrow NOH:CCl\cdot COMe \longrightarrow H_2C_2O_4 + NOH:CCl\cdot NO_2.$$

Chloromethylnitrolic acid, $NOH:CCl\cdot NO_2$, crystallises from chloroform in flattened needles exhibiting a faint yellow reflection, m. p. 101° (decomp.). It can be kept unchanged for some time in sealed vessels, but in the air it decomposes rapidly with evolution of nitrous fumes. It has the normal molecular weight in freezing acetic acid and dissolves readily in ether and, to a moderate extent, in chloroform or carbon tetrachloride; it dissolves also in benzene, but decomposes when the solution is heated. It is acted on by water, undergoing limited decomposition according to the equation: $NOH:CCl\cdot NO_2 = CO_2 + HCl + N_2O$. Its salts are very unstable, and in presence of water undergo quantitative decomposition, yielding nitrous oxide together with the carbonate and chloride of the metal. This decomposition is similar to that occurring with nitrolic acids in presence of water (compare Graul and Hantzsch, Abstr., 1899, i, 187). In presence of acids, chloromethylnitrolic acid is moderately stable. T. H. P.

Synthesis of Secondary *iso*Amyl Alcohol. LOUIS HENRY (*Compt. rend.*, 1907, **145**, 21—25).—By the action of magnesium methyl bromide in ethereal solution on *iso*butylene oxide, neither γγ-dimethylpropyl alcohol nor β-methylbutane-β-ol is formed, but the product consists of β-methylbutane-γ-ol, also formed by the action of magnesium methyl bromide on *iso*butaldehyde, which is isomeric with *iso*butylene oxide. This unlooked-for result is probably due to the preliminary transformation of *iso*butylene oxide into *iso*butaldehyde, since γγ-dimethylpropyl alcohol, a direct product from the oxide, is known to change into the tertiary β-methylbutane-β-ol, but not into the secondary β-methylbutane-γ-ol.

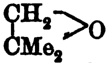
The syntheses of the latter alcohol by the action of zinc methyl on bromoacetyl bromide (Winogradoff, Abstr., 1878, 483) and on chloroacetyl chloride (Bogomotez, *Annalen*, 1881, **209**, 70) are probably to be explained by the reaction of the zinc methyl with the ·COBr and ·COCl groups, forming the compounds $CH_2Br\cdot CMe_2\cdot OZnMe$ and $CH_2Cl\cdot CMe_2\cdot OZnMe$, which by splitting off MeZnCl or MeZnBr form *iso*butylene oxide, the latter then reacting with zinc methyl as with magnesium methyl bromide (compare this vol., i, 670).

Magnesium methyl bromide in ethereal solution reacts with chloroacetone giving the compound $CH_2Cl·CMe_2·OMgBr$, which, on heating in ethereal solution, forms magnesium chlorobromide and *iso*butylene oxide, the latter then reacting with magnesium methyl bromide in the usual way.

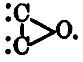
By the action of magnesium methyl bromide (3 mols.) on chloroacetyl chloride (1 mol.), whilst the chief product is *iso*butylene chlorohydrin, $CH_2·Cl·CMe_2·OH$, a very appreciable quantity of β-methylbutane-γ-ol is formed. E. H.

Cetyl Alcohol from the Fat of Dermoid Cysts. FRANZ AMESEDER (*Zeitsch. physiol. Chem.*, 1907, **52**, 121—128. Compare Ludwig, Abstr., 1897, ii, 336).—The compound obtained from the fat of dermoid cysts and described as cetyl alcohol is shown to be an *eicosyl alcohol*, $C_{20}H_{42}O$; it melts at 70° and yields an *acetate*, m. p. 44°, b. p. 220°/3 mm. The acetate when hydrolysed yields 17·3% of acetic acid, and the alcohol when oxidised yields arachidic acid.

J. J. S.

Structural Stability of Ethylene Oxide. LOUIS HENRY (*Compt. rend.*, 1907, **145**, 154—156).—When treated with magnesium methyl bromide, *iso*butylene oxide,  $\begin{matrix}CH_2\\ |\\ CMe_2\end{matrix}\!>\!O$, yields the secondary *iso*amyl alcohol, $CHMe_2·CHMe·OH$, but ethylene oxide gives the primary *n*-butyl alcohol. Hence, contact with magnesium ethyl bromide does not cause ethylene oxide to react as if it had the isomeric constitution $CHMe\!:\!O$. This is due to the stability conferred upon polycarbon nuclei and carbon molecules, in general, by abundance of hydrogen.

T. H. P.

Hydrolysis of the Ethylenic Oxides by Sulphuric Acid. LOUIS HENRY (*Compt. rend.*, 1907, **144**, 1404—1406).—The method of preparing glycerol α-chlorohydrin by the hydrolysis of epichlorohydrin by sulphuric acid is applicable to all the ethylenic oxides containing the group  $\begin{matrix}:C\\ |\\ :C\end{matrix}\!>\!O$. Since the latter can be readily prepared from the monochlorohydrins containing the group $:C(OH)·CCl:$, which are obtained by the application of Grignard's reaction to chloro-ketones containing the group $·CO·CCl:$, or to esters of α-chloro-fatty acids, the method is a convenient one for preparing the α-glycols. In this way, the author has obtained *iso*butylene glycol,

$OH·CMe_2·CH_2·OH$,

β-ethylbutylene-αβ-glycol, $CEt_2(OH)·CH_2·OH$, a crystalline solid, m. p. 46°, b. p. 200—202°/756 mm., *β-methylbutylene-αβ-glycol*, $CMeEt(OH)·CH_2·OH$, a liquid, b. p. 190°/756 mm., *β-iso*amylene glycol, $OH·CMe_2·CHMe·OH$, and *α-methyl-β-amylene glycol*,

$CHEt(OH)·CMe_2·OH$,

a liquid, b. p. 184—185°, prepared from ethyl α-chlorobutyrate. The β-oxides being prepared from the β-glycols by dehydration with sulphuric acid are not affected by the latter reagent. E. H.

The Pinacone from Diethyl Ketone, and its Derivatives formed by the Action of Acids. MAXIMILIAN SAMEC (*Monatsh.*, 1907, 28, 739—765).—An investigation to determine the constitution of the oxide, $C_{10}H_{20}O$, and hydrocarbon, $C_{10}H_{18}$, obtained by Kohn (Abstr., 1905, i, 167) by the action of dilute sulphuric acid on propionepinacone. Diethyl ketone, when reduced with sodium in ethereal solution under an aqueous solution of potassium carbonate, yields, in addition to the pinacone, an analogue of phorone (compare Braun and Kittel, this vol., i, 16), the formation of which was not observed by Kohn (*loc. cit.*).

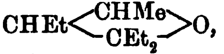
The *phorone* from diethyl ketone is an oil, b. p. 153—155°/20 mm., which does not solidify at −80°. It has the formula

$$\mathrm{CEt_2{:}CMe{\cdot}CEt{:}CMe{\cdot}COEt}$$

or $\mathrm{CEt_2{:}CMe{\cdot}CO{\cdot}CMe{:}CEt_2}$, since it gives acetic, propionic, and pyruvic acids on oxidation, forms an *additive compound* with 2 mols. of bromine, and yields an *oxime*, $C_{15}H_{26}{:}NOH$, a yellowish-brown, crystalline substance, m. p. 52°.

That propionepinacone is undoubtedly a substituted glycol, follows from the fact that it reacts with zinc ethyl with the formation of a *substance*, $\mathrm{EtZn{\cdot}O{\cdot}CEt_2{\cdot}CEt_2{\cdot}OZnEt}$, which is decomposed by water, forming zinc hydroxide and regenerating the pinacone.

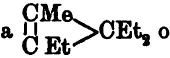
The oxide, $C_{10}H_{20}O$, probably has the formula



$$\mathrm{CHEt}\Big\langle\begin{matrix}\mathrm{CHMe}\\ \mathrm{CEt_2}\end{matrix}\Big\rangle\mathrm{O},$$

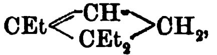
since it neither reacts with zinc ethyl nor gives an oxime, and yields on oxidation with potassium permanganate the following products: an *oxide*, $C_9H_{18}O$, *as*-diethylacetone, diethyl ketone, α-ethylbutyric acid, the *acids*, $C_9H_{18}O_3$, $C_6H_{12}O_3$, $C_8H_{14}O_3$, $C_{10}H_{20}O_4$, acetic and propionic acids, and carbon dioxide. An *alcohol*, $C_{10}H_{22}O$, is obtained by reducing the oxide with sodium in alcoholic solution.

The hydrocarbon, $C_{10}H_{18}$, has either the formula



$$\begin{matrix}\mathrm{CMe}\\ \|\\ \mathrm{C\ Et}\end{matrix}\Big\rangle\mathrm{CEt_2}$$

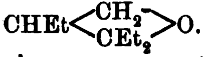
or



$$\mathrm{CEt}\Big\langle\begin{matrix}\mathrm{CH}\\ \mathrm{CEt_2}\end{matrix}\Big\rangle\mathrm{CH_2},$$

since it forms an additive compound with 1 mol. of bromine, yields on reduction a saturated *hydrocarbon*, $C_{10}H_{20}$, and on oxidation the *acids*, $C_6H_{12}O_3$, $C_{10}H_{20}O_4$, and acetic and propionic acids. The relationship existing between these compounds is made clear by the aid of the above formulæ.

The *oxide*, $C_9H_{18}O$, is a liquid, b. p. 180°; it is very similar to the oxide from which it is derived, since it does not combine with bromine, neither does it interact with hydroxylamine, water, zinc ethyl, or sodium. It therefore probably has the formula



$$\mathrm{CHEt}\Big\langle\begin{matrix}\mathrm{CH_2}\\ \mathrm{CEt_2}\end{matrix}\Big\rangle\mathrm{O}.$$

When oxidised with potassium permanganate, it gives the *acids* $C_9H_{18}O_3$ and $C_6H_{12}O_3$.

The *acid*, $C_9H_{18}O_3$, is probably identical with that obtained by Kohn (*loc. cit.*), who assigned to it the formula $C_9H_{16}O_3$.

The *acid*, $C_6H_{12}O_3$, is undoubtedly *α-hydroxy-α-ethylbutyric acid*, since it gives a *barium* salt, $(C_6H_{11}O_3)_2Ba$, and yields diethyl ketone, carbon dioxide, and acetic and propionic acids on oxidation.

The *acid*, $C_8H_{14}O_3$, is probably diethylacetoacetic acid, since it gives a brown turbidity with ferric chloride and is decomposed by dilute sulphuric acid into α-ethylbutyric and acetic acids.

The *acid*, $C_{10}H_{20}O_4$, has either the formula

$$OH\cdot CHMe\cdot CEt_2\cdot CH(OH)\cdot CH_2\cdot CO_2H$$

or $OH\cdot CHMe\cdot C(OH)(CHEt_2)\cdot CH_2\cdot CO_2H$, since it gives a *silver* salt, $C_{10}H_{19}O_4Ag$, and yields diethyl ketone and malonic acid on oxidation. When heated alone, it decomposes into diethyl ketone, acetic acid, and carbon dioxide.

The *alcohol*, $C_{10}H_{22}O$, is a liquid, b. p. 205°. It does not combine with bromine, and gives the iodoform reaction.

The saturated *hydrocarbon*, $C_{10}H_{20}$, is a liquid, b. p. 198°.

W. H. G.

Asymmetric Derivatives of Hexane-αζ-diol; Heptamethylene Glycol. R. Dionneau (*Compt. rend.*, 1907, **145**, 127—129. Compare Abstr., 1906, i, 134).—Bromo-ethers of hexane-αζ-diol are obtained more easily from the dibromo- than from the dialkyloxy-compounds.

ζ-Bromo-α-methoxyhexane, $CH_2Br\cdot[CH_2]_4\cdot CH_2\cdot OMe$, formed together with αζ-dimethoxyhexane by the action of sodium ethoxide on αζ-dibromohexane, is obtained in a 75% yield as a colourless liquid, b. p. 112°/35 mm., D^{21} 1·194, having a slight fruity odour. This forms the *magnesium* derivative, $MgBr\cdot CH_2\cdot[CH_2]_4\cdot CH_2\cdot OMe$, which reacts with bromomethoxymethane yielding *αη-dimethoxyheptane*,

$$CH_2([CH_2]_3\cdot OMe)_2.$$

αη-Dibromoheptane, b. p. 156°/35 mm., is prepared by heating the dimethoxyheptane with hydrobromic acid at 100°, and reacts with sodium phenoxide, forming diphenoxyheptane, m. p. 53°. *αη-Diacetoxyheptane*, formed by the action of silver acetate on the dibromoheptane, is a colourless liquid, b. p. 270°, D^{15} 1·01, and when hydrolysed yields *heptane-αη-diol* (*heptamethylene glycol*), which is obtained in crystals, m. p. 19°, b. p. 172°/35 mm. or 259°/760 mm., and deliquesces on exposure to air.

G. Y.

Direct Hydrogenation of the Anhydrides of Aliphatic Acids. Paul Sabatier and Alphonse Mailhe (*Compt. rend.*, 1907, **145**, 18—21).—When the vapour of acetic anhydride mixed with excess of hydrogen is passed over reduced nickel heated at 180°, there are formed (1) a small quantity of acetaldehyde; (2) ethyl acetate; (3) ethyl alcohol, and (4) acetic acid. The first reaction probably consists in the splitting up of the acetic anhydride molecule, thus: $(COMe)_2O + H_2 = CH_3\cdot CHO + CH_3\cdot CO_2H$. The aldehyde is further hydrogenated to ethyl alcohol, part of which esterifies some of the acetic acid, the water so liberated acting on some of the unaltered acetic anhydride. The first reaction cannot be the direct hydrogenation of acetic anhydride to ethyl acetate, thus: $(COMe)_2O + 2H_2 = CH_3\cdot CO_2Et + H_2O$ (compare Godchot, *Bull. Soc. chim.*, 1907, [iv], 1, 243), followed by decomposition into acetaldehyde and ethyl alcohol, since ethyl acetate is not hydrogenated at 180°. The nickel is not attacked by the acetic acid produced. Similarly, with propionic, methylpropionic, butyric, and methylbutyric anhydrides the main reaction is a decomposition into acid and aldehyde, and this is followed by hydrogenation of the aldehyde and formation of the ester. The proportion of the latter diminishes, whilst that of the aldehyde increases, with the carbon-content of the anhydride. The reaction is the same when reduced copper at 200—210° is substituted for the nickel, but copper being much less active, the principal products are the aldehyde and acid (which attacks copper much more rapidly than nickel). E. H.

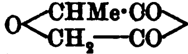
New Derivative of Molybdenum Peroxide. Arrigo Mazzucchelli (*Atti R. Accad. Lincei*, 1907, [v], 16, i, 963—966. Compare this vol., ii, 54).—When barium chloride solution is added to a solution of the compound $MoO_3,(NH_4)_2C_2O_4$ and the crystalline precipitate formed treated with hydrogen peroxide, it yields the *compound* $BaC_2O_4,MoO_4,2\frac{1}{2}H_2O$, which separates from aqueous alcohol in cream-yellow flocks. T. H. P.

Attempts to Prepare Esters of Ortho-Acids. Hans Reitter and A. Weindel (*Ber.*, 1907, 40, 3358—3361. Compare this vol., i, 677).—Attempts have been made to prepare the semi-ortho-ester of malonic acid, $CO_2Et\cdot CH_2\cdot C(OEt)_3$, by the action of alcohol at the ordinary temperature on the hydrochloride of the iminoether of ethyl cyanoacetate (Pinner and Oppenheimer, Abstr., 1895, i, 266). The product actually obtained by fractional distillation under reduced pressure, after the removal of ammonium chloride, contains a molecule of alcohol less than the expected ester, and is probably *ethyl β-diethoxyacrylate*, $C(OEt)_2{:}CH\cdot CO_2Et$. It is a colourless, refractive liquid, b. p. 127·8—128·2°/12 mm., D^{15} 1·035. With an excess of bromine in chloroform solution, it yields ethyl dibromomalonate, and with water at the ordinary temperature it yields ethyl alcohol and ethyl malonate:

$$C(OEt)_2{:}CH\cdot CO_2Et + H_2O = CH_2(CO_2Et)_2 + EtOH.$$

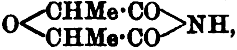
J. J. S.

Intermediate Products in Chemical Reactions. Julius Tafel (*Ber.*, 1907, 40, 3318—3321).—Polemical. A reply to Wohl's contention that intermediate products exist in transformations such as that of fumaric into maleic acid (this vol., i, 583). W. R.

Diglycollic Acid and its Homologues. Émile Jungfleisch and Marcel Godchot (*Compt. rend.*, 1907, 145, 70—73. Compare this vol, i, 471).—By the action of ethyl chloroacetate on the sodium derivative of ethyl glycollate, *diethyl diglycollate*, $O(CH_2\cdot CO_2Et)_2$, b. p. 129—130°/20 mm., is formed, and by saponification gives Heintz's diglycollic acid (*Annalen*, 1867, 144, 91). The interaction of ethyl α-bromopropionate with the sodium derivative of ethyl glycollate, or ethyl chloroacetate with the sodium derivative of ethyl lactate, gives *ethyl methyldiglycollate*, $CO_2Et\cdot CHMe\cdot O\cdot CH_2\cdot CO_2Et$, a liquid insoluble in water, b. p. 122—125°/20 mm., which, by the method previously described, yields the *acid* in crystals, m. p. 30°. When the latter is heated with acetyl chloride, it loses water, forming *methyldiglycollic anhydride*,  $\mathrm{O}\left\langle\begin{array}{l}\mathrm{CHMe\cdot CO}\\ \mathrm{CH_2{-}{-}CO}\end{array}\right\rangle\mathrm{O}$, a syrupy liquid, b. p. 122—125°/25 mm., D^{20} 1·2729, which in contact with water regenerates the acid.

By the prolonged action of concentrated aqueous ammonia on ethyl methyldiglycollate, the *diamide*, $NH_2\cdot CO\cdot CHMe\cdot O\cdot CH_2\cdot CO\cdot NH_2$, is formed in small prisms, m. p. 126°. By heating the latter above its melting point, or by treating a benzene solution of the anhydride with dry ammonia, a substance is formed which seems to be the corresponding *imide*.

When ethyl dilactylate is submitted to the action of cold concentrated aqueous ammonia, it is transformed into *dilactylic diamide*, $O(CHMe\cdot CO\cdot NH_2)_2$, forming thin plates, m. p. 156°; when heated at 160—170°, the latter loses ammonia, forming the *imide*,



$$\mathrm{O}\left\langle\begin{array}{l}\mathrm{CHMe\cdot CO}\\ \mathrm{CHMe\cdot CO}\end{array}\right\rangle\mathrm{NH},$$

which crystallises in large, colourless prisms, m. p. 122°. E. H.

Preparation of Ketone Acetals. ALEXANDER E. ARBUSOFF (*Ber.*, 1907, **40**, 3301—3304. Compare Reitter and Hess, this vol., i, 677).—The author concludes that (1) chemically pure ethyl orthoformate does not react with pure ketones in ether, free from water and alcohol, or by themselves (compare Claisen, Abstr., 1896, i, 463; 1897, i, 188). (2) In the presence, however, of primary alcohols, they react forming ketone acetals and ethyl formate. (3) The alcohol takes therefore an active part in the interaction. (4) Ethyl orthoformate reacts with ketones in the presence of mineral acid, which acts as a catalyst. (5) The reaction proceeds most easily with fatty ketones, less easily with aromatic, and least readily with cyclic, ketones. The examples given in the paper are acetone acetal, acetophenone acetal, and *chloroacetone acetal*; the latter has b. p. 162—163°/760 mm. and 57°/12 mm., D_0^{14} 1·0002. W. R.

Syntheses by Means of Mixed Organo-metallic Derivatives of Zinc. αβ-Acyclic Unsaturated Ketones. EDMOND E. BLAISE and M. MAIRE (*Compt. rend.*, 1907, **145**, 73—75).—The β-hydroxy-aliphatic acids are easily prepared by condensing the esters of α-halogen-aliphatic acids with aldehydes or ketones in the presence of zinc. When these contain a primary or secondary alcohol group, they form acetyl compounds, which are transformed by thionyl chloride into the acid chlorides. The latter react with the mixed organo-metallic derivatives of zinc to form β-acetoxyketones, which on saponification are transformed into the αβ-unsaturated ketones in theoretical yield,

$$OH\cdot CHR\cdot CHR'\cdot CO_2H \longrightarrow OAc\cdot CHR\cdot CHR'\cdot COCl \longrightarrow$$
$$OAc\cdot CHR\cdot CHR'\cdot COR'' \longrightarrow R\cdot CH{:}CR'\cdot COR''.$$

When the β-hydroxy-acid contains a tertiary alcohol group, attempted acetylation results in the dehydration of the acid, but the chloride of the unsaturated acid produced reacts with the organo-metallic derivative to form the corresponding unsaturated ketone (in good yield), except in cases where the fundamental chain of the acid is insufficiently substituted. In the latter instances, the $\cdot COCl$ group is transformed into the tertiary alcohol group, which is further changed by the acid chloride present into an ester, $CH_2\colon CEt\cdot COCl \longrightarrow CH_2\colon CEt\cdot CR_2\cdot O\cdot CO\cdot CEt\colon CH_2$. The above reactions give satisfactory results in a large number of cases, but the authors consider it probable that the acetoxyketones have not the normal constitution.

Magnesium organo-metallic derivatives react with ethyl semi-ortho-oxalate according to the scheme:

$$C(OEt)_3\cdot CO_2Et \longrightarrow CH_2R\cdot C(OEt)_2\cdot C(CH_2R)_2\cdot OH \longrightarrow CH_2R\cdot CO\cdot C(CH_2R)_2\cdot OH \longrightarrow CH_2R\cdot CO\cdot C(CH_2R)\colon CHR,$$

but a large excess (5 mols.) of the organo-magnesium compound is required, and the method only gives ketones of a certain type. With ethyl β-ethoxycrotonate, organo-magnesium compounds do not react in the normal manner, but 1 molecule of the magnesium compound transforms the esteric group into a ketonic group, whilst a second molecule replaces the ethoxy-group by an alkyl:

$$OEt\cdot CMe\colon CH\cdot CO_2Et \longrightarrow CMeR\colon CH\cdot COR.$$

E. H.

Carbohydrate contained in Elm Galls. NAPOLEONE PASSERINI (*Gazzetta*, 1907, 37, i, 386—391).—Fresh elm galls, produced by *Schizoneura ulmi*, contain a colourless or brown, faintly alkaline liquid, having D^{21} 1·06553 and $[\alpha]_D^{21}$ +46·4°. Analysis of one sample gave 84·8% water, 14·54% organic and volatile substances, and 0·66% ash. The amount of solid matter present is 14—20%, consisting principally of a gummy *carbohydrate*, $C_6H_{10}O_5$ (?), which is precipitated by alcohol, softens at 230—240° and swells up at 250—255°, and dissolves sparingly in 98% alcohol, ether, or chloroform; $[\alpha]_D^{20·4}$ 191·8. With water it forms pseudo-solutions, and with nitric acid it yields tartaric and oxalic acids. It probably belongs to the dextrin group, but differs from ordinary dextrin in being precipitable by basic lead acetate solution. Its rotatory power and iodine reaction resemble those of Musculus and Gruber's achroodextrin β.

T. H. P.

Saccharification of Soluble Starch by Extract of Barley. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1907, 145, 80—82).—Extracts of barley convert the most resistant dextrins into maltose; the change is, however, much slower than with malt extract. When the temperature is raised to 45°, the action is incomplete, and a residue of a stable dextrin remains.

N. H. J. M.

Colour Reactions of Lignocellulose. CHARLES F. CROSS, EDWARD J. BEVAN, and JOHN F. BRIGGS (*Ber.*, 1907, 40, 3119—3126. Compare Trans., 1899, 75, 752).—The reactions of phloroglucinol in presence of hydrochloric acid and of dimethyl-*p*-phenylenediamine with certain reactive groups in lignocellulose have been found of value in the localisation of these in the molecule. Phloroglucinol reacts mainly and quantitatively with the lignone complex, but independently of this, in the colour reaction with that part of the molecule which yields furfuraldehyde on treatment with hydrochloric acid; bases, on the other hand, react only with the latter part of the lignocellulose molecule.

The maximum absorption of phloroglucinol by lignocelluloses is determined with the aid of a volumetric method founded on the reaction of furfuraldehyde with phloroglucinol; paper made from wood shavings is a sensitive indicator, giving a coloration with phloroglucinol in 1 : 30,000 solution. The following maximum absorptions of phloroglucinol are given in percentages of the fibres: pine-wood, 6·71, 6·63; jute, 4·23, 4·20, 4·34; wood cellulose (sulphite), 0·75; esparto-cellulose, 0·50; cotton-wool cellulose, 0·20; hydrocellulose, formed by treatment of cotton-wool with hydrochloric acid, 0·42; hydrolignocellulose from jute, 4·45. These results give a method for the estimation of pine-wood fibres which is free from the errors of the colorimetric method. The constitution of the lignone complex of jute is not altered on chlorination or acetylation, as the maximum absorption remains almost unchanged. The increase over the normal maximum absorption of cotton-wool and jute after treatment with hydrochloric acid has no relation to the amount of furfuraldehyde formed (compare Schwalbe, this vol., i, 390).

The intensity of the coloration obtained with pine-wood sawdust and dimethyl-*p*-phenylenediamine hydrochloride in sodium acetate solution increases with the amount of base present, as does also the percentage of base absorbed and not removed by washing with water. The action of phenylhydrazine on lignocelluloses is of the same nature; the phenylhydrazones formed give colour reactions only on prolonged treatment with phloroglucinol and hydrochloric acid, hence the phenylhydrazine must react with the groups which give the coloration with the phenol. In their stability, the phenylhydrazones lie between the derivatives of lignocellulose with mono- and di-amines, which are readily hydrolysed by acids or alkalis, and the compounds with phloroglucinol, which remain unchanged in boiling dilute alkalis.

Lignocelluloses react with hydroxylamine, undergoing a change of colour, which, in general, consists of a partial bleaching; the products give colorations on prolonged treatment with phloroglucinol and hydrochloric acid, but not with aniline or diamines. G. Y.

Cobaltinitrites. KARL A. HOFMANN and O. BURGER (*Ber.*, 1907, 40, 3298—3301).—The surprising stability of the cobaltinitrites would suggest that these salts do not possess the nitrite constitution. If potassium cobaltinitrite is warmed with chloroplatinic acid in alcohol, ethyl nitrite is gradually evolved, but not nitroethane; but this is not conclusive, as it might be a secondary result due to nitrous acid. Also, if the silver salt, obtained by the interaction of ethylammonium cobaltinitrite and silver nitrate, is treated with ethyl iodide, there is a good yield of ethyl nitrite, but nitroethane cannot be detected, from which it may be concluded that the salt has the normal nitrite structure. Ammonium cobaltinitrite (Rosenheim and Koppel, Abstr., 1898, ii, 430), of which the method of preparation is given, when heated evolves 20·39% of its nitrogen in the free state, 6·63% as nitric oxide, and the remainder as nitrate. The nitrogen % corresponds nearly with that required for the decomposition of the 3 mols. of ammonium nitrite.

Ethylammonium cobaltinitrite, $Co(NO_2)_6 \cdot (NH_3Et)_3$, obtained by passing nitrous fumes into an ice-cooled mixture of cobalt carbonate, water, and ethylamine, crystallises in hexagonal, orange plates, decomp. at 131°. Heated at 145°, ethylamine is not evolved, but 18·63—18·87% N and 5·6—6·8% N in the form of nitric oxide is obtained. This % of free nitrogen corresponds again with 3 mols. of ethylammonium nitrite of normal constitution. W. R.

Action of Zinc Ethyl on Nitrosyl Chloride. IWAN BEWAD (*J. pr. Chem.*, 1907, [ii], 76, 62—64. Compare Abstr., 1900, i, 629). —As the nitrosyl group, :NO, of nitrous esters reacts with zinc alkyls in the same manner as does the carbonyl group of such substances as aldehydes or formic esters, it was to be expected that the nitrosyl group of nitrosyl chloride would react with zinc alkyls in the same manner as the carbonyl group of phosgen or of the chloro-anhydrides of carboxylic acids. This has been found to be the case with nitrosyl chloride and zinc ethyl, which react in cooled ethereal solution; treatment of the product with ice-water leading to the formation of β-diethylhydroxylamine in a 44% yield, together with small amounts of ethyl alcohol and ethyl iodide. G. Y.

Preparation of Primary Amino-alcohols. HENRI GAULT (*Compt. rend.*, 1907, 145, 126—127. Compare Bouveault and Blanc, Abstr., 1905, i, 12).—Primary alcohols containing a secondary or tertiary amino-group are obtained by reduction of the corresponding ethyl esters by means of sodium and alcohol. The following alcohols were obtained in this manner in the percentage yields quoted.

β-Diethylaminoethyl alcohol, 50%; β-benzylaminoethyl alcohol, 20%; β-anilinoethyl alcohol, 40—50%; β-methylanilinoethyl alcohol, 30%, together with considerable amounts of methylaniline; γ-diethylaminopropyl alcohol, 40%, together with diethylamine.

Alcohols are not obtained in this manner from ethyl *m*- and *p*-toluidinoacetates, probably in consequence of the formation of insoluble, unreducible sodium derivatives. On treatment with sodium and alcohol, glycine ethyl ester is decomposed into ammonia and acetic acid and does not yield even traces of the amino-alcohol.

G. Y.

Preparation of Aliphatic Thiocyanates, Nitriles, and Nitro-compounds. PAUL WALDEN (*Ber.*, 1907, 40, 3214—3217).—Methyl thiocyanate is obtained in 80—81% yield when methyl sulphate is added slowly and with vigorous shaking to a concentrated aqueous solution of potassium thiocyanate in quantities determined by the equation: $Me_2SO_4 + KSCN = KMeSO_4 + MeSCN$. An 87% yield of ethyl thiocyanate is obtained in a similar manner.

For the preparation of acetonitrile, 1 mol. (65 grams) of potassium cyanide is dissolved in 50—60 grams of water, and 1 mol. of methyl sulphate added in three portions to the solution, which is shaken vigorously and cooled in ice. After the distillation of the nitrile, a second mol. of potassium cyanide is added to the residual liquor, which is then carefully heated in a reflux apparatus; by distillation from a water bath, a further quantity of the nitrile is obtained, the total yield being theoretical. Propionitrile is obtained in a similar manner.

Nitromethane is obtained in 50—57% yield when methyl sulphate (1 mol.) is added to a concentrated aqueous solution of potassium or sodium nitrite (1 mol.), the mixture being shaken and kept cold; when the reaction slackens, a second mol. of the nitrite is added. The mixture is then distilled finally under reduced pressure. Ethyl sulphate reacts in a similar manner, but less energetically than the methyl ester. C. S.

Direct Oxidation of Toluene by Catalysis. PAUL WOOG (*Compt rend.*, 1907, **145**, 124—126).—Coquillon (this Journ., 1873, 1214) found that toluene, when mixed with air and passed over a red-hot spiral of platinum or palladium, is oxidised to benzaldehyde and benzoic acid. The present paper is an extension of this investigation to the direct oxidation of toluene under the influence of various catalysts.

When mixed with air and passed over meerschaum, which has been impregnated with a platinum salt and reduced, toluene vapour is oxidised to carbon dioxide and water, with development of sufficient heat to raise the mass to incandescence. The reaction does not take place if the tube containing the meerschaum is maintained below the b. p. of toluene. Benzaldehyde is formed when the mixture of toluene and air is passed over pumice impregnated with ferric oxide; the best yields are obtained by heating the toluene at 90° and the catalyst at 280°. Under similar conditions, benzaldehyde is formed in presence of nickel oxide at 150°, at 230° phenolic products are obtained, whilst if the tube is heated at 270°, the oxide becomes incandescent. With copper oxide as the catalyst, small amounts of benzaldehyde are formed at 180—260°, but the greater part of the toluene is completely oxidised; incandescence is observed at 250°. With manganese dioxide, the oxidation is complete; the catalyst becomes incandescent at 250°. In presence of coke, toluene is oxidised at 200°, yielding small amounts of benzaldehyde together with larger quantities of benzoic acid, which is formed abundantly at 370°. The coke does not become incandescent. G. Y.

Condensations under the Influence of Sodium. PAUL SCHORIGIN (*Ber.*, 1907, **40**, 3111—3118).—Since in the Wurtz synthesis of hydrocarbons, two positive groups combine in consequence of the elimination of halogen by sodium, and, on the other hand, two negative benzoyl groups unite to form benzil in Klinger's synthesis of this substance by the action of sodium amalgam on benzoyl chloride (Abstr., 1883, 920), it was to be expected that the action of sodium on a mixture of an alkyl haloid, RX, and benzoyl chloride would lead to the formation of a ketone, R·COPh, rather than to that of the hydrocarbon, R·R, and benzil. The interaction of *iso*butyl bromide, benzoyl chloride, and sodium in benzene solution is found to be more complicated, the product obtained on distillation of the reaction mixture being δ-phenyl-*βζ*-dimethyl-Δ^{γ}-heptene, which is considered to be formed in the four stages: (1) $C_4H_9Br + COPhCl + 2Na =$

$NaCl + NaBr + COPh\cdot C_4H_9$; (2) $COPh\cdot C_4H_9 + C_4H_9Br + 2Na = NaBr + ONa\cdot CPh(C_4H_9)_2$; (3) $ONa\cdot CPh(C_4H_9)_2 + COPhCl = NaCl + COPh\cdot O\cdot CPh(C_4H_9)_2$, and (4) $COPh\cdot O\cdot CPh(C_4H_9)_2 =$

$$CH_2Pr^\beta\cdot CPh{:}CHPr^\beta + C_6H_5\cdot CO_2H.$$

The intermediate formation of the sodium derivative of the tertiary alcohol is the more probable, since phenyldi*iso*amylcarbinol is formed by the action of *iso*amyl bromide on ethyl benzoate in presence of sodium. The fourth stage takes place during the distillation of the reaction mixture (compare Krafft, Abstr., 1884, 571). The unsaturated hydrocarbon may be formed, however, at least partially, by direct loss of water from the tertiary alcohol, since phenyldi*iso*amylcarbinol decomposes partially in this manner when distilled in a vacuum. Attempts to prepare phenyldi*iso*butylcarbinol by Grignard's reaction led to the formation of phenyl*iso*butylcarbinol, probably in consequence of reduction of the ketone formed in the first stage by the second mol. of magnesium *iso*butyl bromide.

δ-Phenyl-βζ-dimethyl-Δγ-heptene, $CHPr^\beta{:}CPh\cdot CH_2Pr^\beta$, is a colourless oil, b. p. 110—112°/10 mm. or 124—126°/20 mm., $D_4^{16\cdot5}$ 0·8731 (corr.), n_D^{25} 1·49762, and forms an *additive compound* with bromine.

*Phenyldi*iso*amylcarbinol*, $OH\cdot CPh(C_5H_{11})_2$, formed by the action of sodium on a mixture of *iso*amyl bromide and ethyl benzoate in ethereal solution, or of magnesium *iso*amyl bromide on methyl benzoate, is a colourless, viscid oil, b. p. 163—165°/14 mm. (corr.), D_4^0 0·9349—0·9365 (corr.), D_4^{17} 0·9210—0·9213 (corr.), $n_D^{24\cdot5}$ 1·49373, n_D^{27} 1·49288; on repeated distillation in a vacuum, it is decomposed almost entirely into water and the unsaturated *hydrocarbon*,

$$CH_2Pr^\beta\cdot CH{:}CPh\cdot CH_2\cdot CH_2Pr^\beta,$$

which is formed also by heating phenyldi*iso*amylcarbinol with acetic anhydride. It is obtained as a mobile, colourless liquid, b. p. 153—155°/18 mm., D_4^0 0·8859 (corr.), D_4^{26} 0·8666 (corr.), $n_D^{26\cdot5}$ 1·49913, and forms an *additive compound* with bromine.

Phenyl*iso*butylcarbinol, formed by the action of magnesium *iso*butyl bromide on methyl benzoate or benzoyl chloride, has the properties described by Klages (Abstr., 1904, i, 567). G. Y.

Action of Some Esters of α-Iodo-fatty Acids on Magnesium Aniline and *o*-Toluidine Iodides. F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1907, **144**, 1437—1438. Compare Bodroux, Abstr., 1905, i, 585, 643).—When ethyl iodoacetate is allowed to act on magnesium aniline iodide in presence of sufficient ether to keep the latter in solution, a similar reaction to that observed with the toluidine compound occurs, *iodoacetanilide* being formed in white needles, m. p. 143—144°, thus:

$$CH_2I\cdot CO_2Et + 2NHPh\cdot MgI \longrightarrow CH_2I\cdot C(NHPh)_2\cdot O\cdot MgI \longrightarrow CH_2I\cdot CO\cdot NHPh.$$

By the action of ethyl α-iodopropionate and α-iodobutyrate on magnesium aniline iodide and magnesium *o*-toluidine iodide, the authors have obtained *α-iodopropionanilide*, $CHMeI\cdot CO\cdot NHPh$, m. p. 135—136°; *α-iodopropion-*o*-toluidide*, $CHMeI\cdot CO\cdot NH\cdot C_6H_4Me$, m. p. 148°; *α-iodobutyranilide*, $CH_2Me\cdot CHI\cdot CO\cdot NHPh$, m. p. 126—127°, and *α-iodobutyr-*o*-toluidide*, $CH_2Me\cdot CHI\cdot CO\cdot NH\cdot C_6H_4Me$, m. p.

138—139°, all of which crystallise in white needles, which slowly become yellow in the light. E. H.

Action of Halogen Derivatives of Acetone on Some Aromatic Amines. A. RICHARD (*Compt. rend.*, 1907, **145**, 129—131).—Vladesco found that methyl α-chloroethyl ketone reacts with aniline and methylaniline, forming 2 : 3-dimethyl- and 1 : 2 : 3-trimethylindole respectively (Abstr., 1892, 810). The author has confirmed these results and has obtained 2 : 3 : 5-trimethylindole by the action of methyl α-chloro- or α-bromo-ethyl ketone on *p*-toluidine. The action of chloro- or bromo-acetone on aniline leads, on the other hand, to the formation of a *hydrate* of anilinoacetone, which, when boiled in aqueous solution and dried, yields the anhydrous *compound*

$$NHPh{\cdot}CH_2{\cdot}COMe.$$

The three *toluidinoacetones* are prepared in the same manner.

G. Y.

Partial Reduction of 2:6- and 2:4-Dinitrotoluenes by Electrolytic Methods. KURT BRAND and H. ZÖLLER (*Ber.*, 1907, **40**, 3324—3334. Compare Abstr., 1906, i, 80).—2 : 2′-*Dinitro*-6 : 6′-*azoxytoluene*, $NO_2{\cdot}C_6H_3Me{\cdot}N_2O{\cdot}C_6H_3Me{\cdot}NO_2$, is obtained when 2 : 6-dinitrotoluene is reduced electrolytically in faintly alkaline solution, using a dilute alcoholic solution of sodium acetate mixed with ethyl acetate as the cathode liquid, and hot saturated sodium carbonate as the anode liquid. It crystallises from benzene in glistening, yellow needles, m. p. 187°. When heated for three to four hours on the water-bath with concentrated sulphuric acid, the azoxy-compound is transformed into 2 : 2′-*dinitro*-3-*hydroxy*-6 : 6′-*azotoluene*, $OH{\cdot}C_6H_2Me(NO_2){\cdot}N_2{\cdot}C_6H_3Me{\cdot}NO_2$, which crystallises from alcohol in slender, yellow needles, m. p. 222°. The *sodium* salt crystallises in red needles, and also the *acetyl* derivative, $C_{16}H_{15}O_6N_4$, m. p. 161°.

2 : 2′-Dinitro-4 : 4′-azoxytoluene, m. p. 164° (compare Weyprecht, *Inaug. Diss. Giessen*, 1902), is produced by the reduction of 2 : 4-dinitrotoluene under similar conditions. Its constitution follows from its synthesis from 2-nitro-4-hydroxylaminotoluene and 2-nitro-4-nitrosotoluene in alkaline solution.

When 2 : 6- and 2 : 4-dinitrotoluenes are reduced in strongly acid solution in the presence of cupric chloride, using lead as the anode and copper or nickel gauze as cathode, the products are respectively 2-nitro-6-aminotoluene and 2-nitro-4-aminotoluene.

A 50—60% yield of pure 2-*nitro*-6-*hydroxylaminotoluene*,

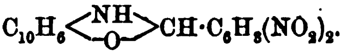
$$NO_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}OH,$$

is formed when 2 : 6-dinitrotoluene is reduced in the presence of sodium acetate, acetic acid, and alcohol, using as cathode a lead coil through which cold water is passed, so that the temperature remains at 40—50°; voltage 14. The product is isolated by the addition of ice, and may be crystallised from benzene. It forms glistening, yellow crystals, m. p. 115°. With sodium hydroxide solution, it yields mainly 2 : 2′-dinitro-6 : 6′-azoxytoluene. When heated, it loses water, yielding dinitroazotoluene, and when oxidised with ferric chloride and sodium acetate in aqueous alcoholic solution it yields 2-*nitro*-6-*nitrosotoluene*, $NO_2\cdot C_6H_3Me\cdot NO$, which crystallises from benzene in colourless needles, melting at 117^{c} to a green liquid. Concentrated sulphuric acid converts the hydroxylamino-compound into 2-*nitro*-6-*amino*-3-*hydroxytoluene*, $NO_2\cdot C_6H_2Me(OH)\cdot NH_2$, which crystallises from alcohol in compact, reddish-brown needles, m. p. 201°. The *diacetyl* derivative, $C_{11}H_{12}O_5N_2$, crystallises in colourless needles, m. p. 127—128°. The formation of a diacetyl derivative indicates that the hydroxyl group is in the para-position with respect to the amino-group, since if it were in the ortho-position, acetic anhydride would cause the elimination of water and the formation of a methylbenzoxazole derivative. 3-*Chloro*-2-*nitro*-6-*aminotoluene*, $NO_2\cdot C_6H_2MeCl\cdot NH_2$, obtained by heating the hydroxylamino-compound with concentrated hydrochloric acid, crystallises from light petroleum in yellow needles, m. p. 96°. Its *acetyl* derivative has m. p. 158—160°. In the formation of the 3-chloro-derivative a small amount of the isomeric 5-chloro-2-nitro-6-aminotoluene appears to be formed. The position of the chlorine in the 3-chloro-derivative has been established by removal of the amino-group and oxidation of the chloronitrotoluene to 3-chloro-2-nitrobenzoic acid, m. p. 235°.

2-*Nitro*-4-*hydroxylaminotoluene*, $C_7H_8O_3N_2$, obtained by the reduction of 2 : 4-dinitrotoluene in nearly neutral solution, separates from benzene in compact, yellow crystals, m. p. 99°. When oxidised, it yields 2-*nitro*-4-*nitrosotoluene*, $C_7H_6O_3N_2$, in the form of colourless needles, melting at 87° to a green liquid, and when heated with concentrated hydrochloric acid it forms 3-*chloro*-2-*nitro*-4-*aminotoluene*, $C_7H_7O_2N_2Cl$, as pale yellow needles, m. p. 63°; the *acetyl* derivative has m. p. 123—124°. The position of the chlorine has been established by removal of the amino-group and subsequent oxidation to 3-chloro-2-nitrobenzoic acid. 5-Chloro-2-nitro-4-aminotoluene, obtained as a by-product in the preparation of the 3-chloro-derivative, has m. p. 131° (Claus and Davidsen, Abstr., 1892, 172, gave 129·5°).

J. J. S.

New Derivatives of 2 : 4-Dinitrobenzaldehyde. FRANZ SACHS and WLADIMIR BRUNETTI (*Ber.*, 1907, 40, 3230—3235).—The 2 : 4-dinitrobenzylideneaminonaphthols are sparingly soluble, crystalline compounds, and are obtained by the interaction of their components in acetic acid solution. They resemble one another in their behaviour towards mineral acids, solubility in alkali hydroxides, and colour reactions with alcoholic alkalis, with the exception of 2 : 4-*dinitrobenzylidene*-1-*amino*-β-*naphthol*, m. p. 201—202°, which does not possess these properties and to which is ascribed the formula



$$C_{10}H_6{<}\begin{smallmatrix}NH\\O\end{smallmatrix}{>}CH\cdot C_6H_3(NO_2)_2.$$

2 : 4-*Dinitrobenzylidene*-α-*naphthylamine*, m. p. 201—203°, forms slender, orange, monoclinic prisms, and the corresponding *derivative* of β-naphthylamine, m. p. 197—199°, yellow, microcrystalline needles.

2′ : 4′-*Dinitrobenzylidene*-7-*amino*-β-*naphthol*, m. p. 189° (decomp.), separates from acetone in yellow needles, which darken by exposure to light; the solution in alcoholic alkalis is dark red. The *methyl ether* has m. p. 206—207°.

2′ : 4′-*Dinitrobenzylidene*-4-*amino-a-naphthol*, m. p. 216° (decomp.), forms reddish-brown needles and develops an intense blue coloration with alcoholic alkalis. The *acetate*, m. p. 210°, forms yellow, hexagonal prisms.

2′ : 4′-*Dinitrobenzylidene-3-amino-β naphthol*, m. p. 204° (decomp.), forms yellow needles and gives a reddish-brown coloration with alcoholic potassium hydroxide; the *benzoate* has m. p. 243° (decomp.).

2′ : 4′-*Dinitrobenzylidene-5-amino-β-naphthol*, m. p. 201° (decomp.), yields a dark red coloration with alcoholic alkalis. 2′ : 4′-*Dinitrobenzylidene-5-amino-a-naphthol* has m. p. 219° (decomp.), and alcoholic alkalis develop a dark violet, whilst the corresponding *derivative* of 8-amino-β-naphthol, m. p. 216° (decomp.), yields a pure violet, coloration.

C. S.

Derivatives of Triphenylcarbinol. ADOLF VON BAEYER [and, in part, ALFONS VON BENTHEIM and CARL DIEHL] (*Annalen*, 1907, **354**, 152—204).—A systematic investigation of the derivatives of triphenylcarbinol has been undertaken with the object of explaining the many obscure points met with in the study of triphenylcarbinol (Abstr., 1902, i, 380, 769; 1903, i, 811; 1904, i, 308, 786, 898; 1905, i, 281, 358). The present paper deals with derivatives of triphenylcarbinol containing not more than one hydroxyl or amino-group in each benzene nucleus. Such substances the author terms unitary derivatives, whilst binary and ternary derivatives are such as contain two and three substituting groups respectively in at least one of the benzene nuclei.

It was shown previously (Baeyer and Löhr, Abstr., 1890, 1141; Baeyer and Villiger, Abstr., 1904, i, 308, 786) that whilst *p*-aminotriphenylcarbinol forms a dye salt, this is only orange in colour and cannot be reckoned as a true aniline dye. In agreement with this, Bistrzycki and Herbst (Abstr., 1903, i, 639) found that diphenylquinomethane, which the present author has termed fuchsone, formed by the elimination of water from *p*-hydroxytriphenylcarbinol, has the same orange colour. On the other hand, Pechmann stated (Abstr., 1881, 96) that *p*-hydroxydiphenylphthalide forms a violet solution in alkalis. This was considered (Abstr., 1905, i, 281) to point to a chromophoric action of the lactone grouping, but it is found now that the violet colour observed by Pechmann was caused by the presence of phenolphthalein and that pure *p*-hydroxydiphenylphthalide is colourless in alkaline solution. If boiled in sodium carbonate solution, *p*-hydroxydiphenylphthalide becomes yellow, which must be ascribed to the formation of the sodium fuchsonecarboxylate, $O:C_6H_4:CPh\cdot C_6H_4\cdot CO_2Na$, since the solution becomes again colourless on addition of an alkali.

Excluding, as is done in this paper, any consideration of the acid salts of the phenolic derivatives, there are only two coloured monohydroxy- and monoamino-triphenylcarbinols: fuchsone, $CPh_2:C_6H_4:O$, and fuchsoneimonium chloride, $CPh_2:C_6H_4:NH_2Cl$. Fuchsones are formed from unitary dihydroxy- and diamino-triphenylcarbinols only if at least one of the substituting groups is in the *p*-position. In the case of the dihydroxy-compounds, the formation of the fuchsone takes place with varying ease according to the position of the second substituting group; *p*-hydroxyfuchsone (benzaurin) is formed immediately as a yellow precipitate on addition of acetic acid to the colourless alkaline solution of 4 : 4′-dihydroxytriphenylcarbinol, whereas the 2 : 4′- and 3 : 4′-derivatives yield white precipitates, which are transformed into the yellow *o*- and *m*-hydroxyfuchsones only when warmed or treated with a mineral acid. These fuchsones have corresponding stabilities, benzaurin forming a violet alkaline solution which becomes colourless only on addition of a large excess of alkali, whilst the bluish-red and blood-red alkaline solutions of the *o*- and *m*-hydroxyfuchsones respectively are readily decolorised. Although the quinone groupings of these substances differ only in degree and not fundamentally, only benzaurin gives a characteristic absorption spectrum.

The unitary dihydroxydiphenylphthalide is phenolphthalein, the violet solution of which in aqueous sodium carbonate must contain the disodium salt, $O{:}C_6H_4{:}C(C_6H_4{\cdot}ONa){\cdot}C_6H_4{\cdot}CO_2Na$, since its absorption spectrum is identical with that of alkaline benzaurin,

$$O{:}C_6H_4{:}CPh{\cdot}C_6H_4{\cdot}ONa.$$

Further proof that the lactone grouping of the phthaleins is not chromophoric is found in the colourless alkaline solution of 3 : 3′-dihydroxyditolylphthalide.

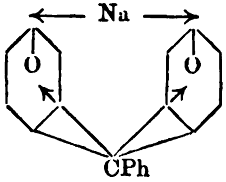
Of the six possible unitary tetramethyldiaminotriphenylcarbinols, only the 4 · 4′-compound yields a dye, malachite-green, when treated with cold dilute hydrochloric acid. The 3 : 4′-compound forms an orange fuchsoneimonium chloride with cold or hot dilute or concentrated hydrochloric acid, whilst the 2 : 4′-compound forms a yellow fuchsoneimonium chloride only with the concentrated or hot dilute acid, remaining colourless when treated with the cold dilute acid; the *o*-amino-group acts as an antiauxochrome. The absorption spectrum of Doebner's violet, the parent substance of malachite-green, is identical with that of alkaline benzaurin; these substances must have corresponding constitutions, although, according to the usual formulæ, the salt formation takes place at different parts of the molecules: $ONa{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}O$, $NH_2{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}NH_2Cl$.

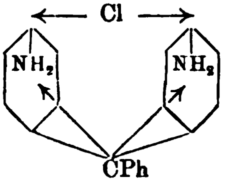
Of the ten possible unitary trihydroxytriphenylcarbinols, only the 4 : 4′ : 4″-form, which changes spontaneously into the 4 : 4′-dihydroxyfuchsone, aurin, is known. Aurin forms a violet solution in alkalis, becoming decolorised on addition of an excess of the alkali; the spectrum of the violet solution resembles that of benzaurin, the absorption bands being displaced slightly towards the violet.

Of the ten possible forms of unitary triaminotriphenylcarbinols, seven have been prepared in various degrees of methylation. Dyes, pararosaniline and *o*-aminomalachite-green, are obtained from the 4 : 4′ : 4″- and 2 : 4′ : 4″-forms; the 2 : 3′ : 4″-compound forms a yellow fuchsoneimonium chloride with hot dilute hydrochloric acid, but is colourless in cold dilute, and almost so in concentrated, acid, whilst the 2 : 2′ : 4″-compound is coloured only very slightly by the concentrated, or hot dilute acid. The compounds which do not contain a para-substituting group do not form coloured hydrochlorides.

As the absorption spectrum of pararosaniline is identical with that of alkaline aurin, the constitutions of these two substances must resemble one another in the same manner as those of Doebner's violet and alkaline benzaurin.

The cause of the colour of the aniline and aurin dyes is discussed and considered to be an oscillation between two forms expressed by the schemes :


Sodium benzaurin.


Doebner's violet.

o-Hydroxytriphenylcarbinol, $C_{19}H_{16}O_2$, prepared by Grignard's reaction from *o*-methoxybenzoic acid and bromobenzene, crystallises in colourless, rectangular plates or prisms, m. p. 140·5°, gives with concentrated sulphuric acid in glacial acetic acid solution a cherry-red coloration which disappears on addition of water, forms a sparingly soluble, crystalline *sodium* salt, yields 9-phenylxanthen when distilled in a vacuum, and is reduced by zinc dust in boiling glacial acetic acid solution, forming *o-hydroxytriphenylmethane*, $C_{19}H_{16}O$, which crystallises from a mixture of benzene and light petroleum in colourless spears, m. p. 124°, or from alcohol in needles, m. p. 76°, containing alcohol of crystallisation.

Diphenyl-o-anisylcarbinol, $C_{20}H_{18}O_2$, prepared by Grignard's reaction from methyl salicylate and bromobenzene, crystallises in colourless, rhombic plates, m. p. 128—129°, gives an intense cherry-red coloration with sulphuric and glacial acetic acids, differs from the para-compound in remaining unchanged when heated with glacial acetic and dilute sulphuric acids, and on treatment with hydrogen chloride in ethereal solution yields the *carbinyl chloride*, $C_{20}H_{17}OCl$, which crystallises in needles, m. p. 126° (decomp.), and is reconverted into the carbinol on exposure to air. The *anilide*, formed by the action of aniline on the carbinyl chloride in ethereal solution, crystallises in hard cubes, m. p. 151°. *Diphenyl-o-anisylmethane*, $C_{20}H_{18}O$, formed by heating the carbinol with zinc dust and glacial acetic acid, crystallises in colourless rhombohedra, m. p. 114°.

m-*Hydroxytriphenylcarbinol* crystallises in prisms, m. p. 147—148°, gives a transient, brownish-red coloration with sulphuric and glacial acetic acids, and is decomposed when boiled with concentrated hydrochloric acid. *Diphenyl*-m-*anisylcarbinol* separates from ether in large, regular crystals, m. p. 88°. m-*Hydroxytriphenylmethane* forms colourless prisms, m. p. 106°.

o-Hydroxydiphenylphthalide, $C_{20}H_{14}O_3$, formed by fusing *o*-benzoylbenzoic acid with phenol and treatment of the product with concentrated sulphuric acid, crystallises in prisms, m. p. 167°.

2-*Hydroxy-5-methyldiphenylphthalide* (o-*hydroxyphenyltolylphthalide*), $C_{21}H_{16}O_3$, prepared by the action of concentrated sulphuric acid on a mixture of *p*-cresol and *o*-benzoylbenzoic acid (compare Drewsen, Abstr., 1882, 1098; Meyer and Hoffmeyer, Abstr., 1892, 970), forms colourless prisms, m. p. 226°, gives an emerald-green coloration with concentrated sulphuric acid, and dissolves in moderately concentrated alkalis on heating; on cooling, the *alkali* salt crystallises in small needles.

m-Dimethylaminotriphenylcarbinol, $C_{21}H_{21}ON$, prepared by Grignard's reaction from methyl *m*-dimethylaminobenzoate and bromobenzene, crystallises in colourless plates, m. p. 110°, gives a slight yellow coloration with fuming hydrochloric acid, and dissolves in concentrated sulphuric acid, forming a colourless solution; the *hydrochloride*, $C_{21}H_{21}ON,HCl$, crystallises in colourless leaflets, m. p. 181° (decomp.). The *hydrochloride* of the *carbinyl chloride*, $C_{21}H_{20}NCl,HCl$, m. p. 154° (decomp.), is converted into the hydrochloride of the carbinol by the action of moist air, and yields hydrogen chloride and a brown, amorphous *mass* when heated in a current of hydrogen. The *methyl ether*, $C_{22}H_{23}ON$, prepared by the action of sodium methoxide on the carbinyl chloride hydrochloride, crystallises in rhombic plates and prisms, m. p. 81°.

2 : 4′-*Dihydroxytriphenylcarbinol*, $C_{19}H_{16}O_3$, formed from 2 : 4′-dihydroxybenzophenone, m. p. 150—151° (143—144°: Michael, Abstr., 1884, 311), and bromobenzene by Grignard's reaction, crystallises in colourless prisms, m. p. 143° (decomp.), dissolves to a colourless solution in alkalis, is precipitated unchanged by acetic acid, and gives a blood-red coloration with concentrated sulphuric acid. o-*Hydroxyfuchsone*, $C_{19}H_{14}O_2$, formed from the dihydroxycarbinol at 150°, crystallises in orange prisms, m. p. 204—205°, forms bluish-red alkaline solutions which rapidly become colourless in consequence of the formation of the carbinol, and with sulphuric acid gives the same coloration as the carbinol.

3 : 4′-Diaminobenzophenone has m. p. 131—132° (121—122°: Gattermann and Rüdt, Abstr., 1894, i, 599). 3 : 4′-Dihydroxybenzophenone has m. p. 205—206° (200°: Gattermann and Rüdt, *loc. cit*).

3 : 4′-*Dihydroxytriphenylcarbinol*, m. p. 155—160° (decomp.), formed from 3 : 4′-dihydroxybenzophenone and bromobenzene by Grignard's reaction, was not purified. It gives an orange-red coloration with sulphuric acid, and when heated at 150° yields m-*hydroxyfuchsone*, $C_{19}H_{14}O_2$, which crystallises from acetone in orange prisms, m. p. 183°, or from chloroform in crystals, m. p. 105—110° (decomp.), containing chloroform, and behaves towards alkalis and concentrated sulphuric acid in the same manner as the *o*-compound.

Phenyldi-o-anisylcarbinol, $C_{21}H_{20}O_3$, formed from *o*-iodoanisole and methyl benzoate, crystallises in rhombic plates, m. p. 115°, gives a brownish-violet coloration with sulphuric and glacial acetic acids, and forms a yellow solution when heated with glacial acetic acid. *Phenyldi-o-anisylmethane*, $C_{21}H_{20}O_2$, crystallises in colourless prisms, m. p. 106°, and has an odour resembling that of guaiacol.

3 : 3′-*Dihydroxytriphenylcarbinol*, $C_{19}H_{16}O_3,C_2H_6O$, m. p. below 100° (decomp.), formed from 3 : 3′-dihydroxybenzophenone, m. p. 170° (162—164°: Gattermann and Rüdt, *loc. cit.*) and bromobenzene, gives a Bordeaux-red coloration with concentrated sulphuric acid.

Phenyldi-m-*anisylcarbinol*, $C_{20}H_{21}O_3$, from *m*-iodoanisole and methyl benzoate, crystallises in rhombic leaflets, m. p. 82—83°, and gives a Bordeaux-red coloration with sulphuric acid in glacial acetic acid solution.

Di-*m*-nitroditolylphthalide, m. p. 157—158° (132°: Limpricht, Abstr., 1898, i, 323), yields 3 : 3′-diaminoditolylphthalide, m. p. 197° (192° : Limpricht, *loc. cit.*), which, when treated with amyl nitrite in concentrated sulphuric acid solution, yields a crystalline *diazosulphate*, which decomposes suddenly when heated. Di-*m*-hydroxyditolylphthalide, $C_{22}H_{18}O_4$, formed by heating the diazosulphate with water at 60°, crystallises in colourless prisms, m. p. 206°, and is colourless in alkaline solution.

m-*Dimethylaminobenzophenone*, $C_{15}H_{15}ON$, formed by the action of methyl sulphate and sodium hydroxide on *m*-aminobenzophenone, is isolated in the form of its *methiodide*, $C_{16}H_{18}ONI$, which crystallises in slender needles, and when heated at 205° loses methyl iodide and yields the *base*, crystallising in slightly yellow plates, m. p. 47°. m-*Dimethylaminobenzhydrol*, $C_{15}H_{17}ON$, prepared by reduction of the ketone with sodium amalgam in alcoholic solution, crystallises in colourless needles, m. p. 102°.

p-Dimethylaminobenzophenone (Doebner and Weiss, Abstr., 1882, 176) is obtained in good yields by the action of methyl sulphate on *p*-aminobenzophenone.

3 : 4′-*Tetramethyldiaminobenzophenone*, $C_{17}H_{20}ON_2$, prepared by heating 3 : 4′-diaminobenzophenone with methyl alcohol at 140—145°, separates from alcohol or ether in brownish-yellow crystals, m. p. 77—78·5°; the *hydrochloride* crystallises in colourless needles, m. p. 278—280° (decomp.); the *platinichloride*, $C_{17}H_{20}ON_2,H_2PtCl_6,H_2O$, forms golden plates, darkens at 100°, and decomposes at 200°. 3 : 4′-*Tetramethyldiaminobenzhydrol*, $C_{17}H_{22}ON_2$, prepared by reduction of the ketone with sodium amalgam, crystallises in colourless needles, m. p. 100—101°, gives with concentrated sulphuric acid a yellow, or with hot glacial acetic acid a yellowish-green, coloration, and forms colourless solutions in other mineral acids.

Di-*m*-nitrodiphenylmethane has m. p. 180°, and di-*m*-nitrobenzophenone, m. p. 160°; Gattermann and Rüdt (*loc. cit.*) give the m. p.'s 172° and 151°. 3 : 3′-*Tetramethyldiaminobenzophenone*, $C_{17}H_{20}ON_2$, prepared by the action of methyl sulphate on the diamino-compound, crystallises from dilute alcohol in yellow prisms, m. p. 59—60°, and forms colourless solutions in dilute or concentrated acids. 3 : 3′-*Tetramethyldiaminobenzhydrol*, $C_{17}H_{22}ON_2$, crystallises in prisms, m. p. 72—73°, and dissolves to colourless solutions in acids.

2 : 4′-*Tetramethyldiaminotriphenylcarbinol*, $C_{23}H_{26}ON_2$, prepared from *p*-dimethylaminobenzophenone and magnesium *o*-dimethylaminophenyl iodide (compare Abstr., 1905, i, 766), separates from alcohol in colourless crystals, m. p. 169·5—170°, and dissolves in glacial acetic acid forming a colourless solution which becomes dark green and, finally, yellow when heated.

2 : 4′-*Tetramethyldiaminotriphenylcarbinyl chloride dihydrochloride*, $C_{23}H_{27}N_2Cl_3$, crystallises in yellow needles, decomp. at 227°, and is unstable in moist air. The *stannichloride* is red.

3 : 4′-*Tetramethyldiaminotriphenylcarbinol*, $C_{23}H_{26}ON_2$, prepared from 3 : 4′-tetramethyldiaminobenzophenone and magnesium phenyl bromide, crystallises in colourless prisms, m. p. 140°.

3 : 4′-*Tetramethyldiaminotriphenylmethane*, $C_{23}H_{26}N_2$, prepared by reduction of the carbinol with zinc dust and hydrochloric acid in presence of hydrogen iodide, forms irregular crystals, m. p. 83—84°.

2 : 2′-*Tetramethyldiaminotriphenylcarbinol*, $C_{23}H_{26}ON_2$, prepared from methyl benzoate and *o*-iododimethylaniline, or from 2 : 2′-tetramethyldiaminobenzophenone and bromobenzene, by Grignard's reaction, crystallises in colourless prisms, m. p. 105°, forms colourless solutions in acids, and does not give a coloration with stannic chloride or when dissolved in glacial acetic acid containing hydrogen bromide, and poured into water, but gives a transient blue coloration on treatment with phosphorus pentachloride in chloroform solution.

2 : 3′-*Tetramethyldiaminotriphenylcarbinol*, $C_{23}H_{26}ON_2$, from *o*-iododimethylaniline and *m*-dimethylaminobenzophenone, crystallises in colourless plates, m. p. 183—184°, and dissolves in glacial acetic acid, forming a colourless solution becoming yellowish-green when heated.

3 : 3′-*Tetramethyldiaminotriphenylcarbinol*, from 3 : 3′-tetramethyldiaminobenzophenone and magnesium phenyl bromide, separates from ether in crystalline crusts, m. p. 128—129°, and gives a yellow coloration with glacial acetic acid, mineral acids, or stannic chloride.

3 : 4′ : 4″-*Hexamethyltriaminotriphenylmethane*, $C_{25}H_{31}N_3$, prepared by condensation of dimethylaniline with 3 : 4′-tetramethyldiaminobenzhydrol in presence of zinc chloride, crystallises in colourless prisms, m. p. 153—154°, is superficially oxidised by air, and on treatment with lead dioxide yields the *carbinol*, which dissolves in cold alcohol or cold dilute hydrochloric acid, forming colourless solutions becoming blue when heated; it becomes blue also when exposed to air containing carbon dioxide.

2 : 2′ : 4″-*Hexamethyltriaminotriphenylcarbinol*, $C_{25}H_{31}ON_3$, from *o*-iododimethylaniline and methyl *p*-dimethylaminobenzoate, forms rhombic crystals, m. p. 172—173°.

2 : 3′ : 4″-*Hexamethyltriaminotriphenylcarbinol*, prepared from *o*-iododimethylaniline and 3 : 3′-tetramethyldiaminobenzophenone, crystallises in rhombic plates, m. p. 148—150°.

2 : 2′ : 2″-*Hexamethyltriaminotriphenylcarbinol*, prepared from *o*-iododimethylaniline and 2 : 2′-tetramethyldiaminobenzophenone, or from *o*-iododimethylaniline and methyl dimethylanthranilate, or *o*-iododimethylaniline and ethyl orthocarbonate, crystallises in prisms or plates, m. p. 107—108°, forms colourless solutions in acids, and does not give Bassett's reaction.

2 : 2′ : 3″-*Hexamethyltriaminotriphenylcarbinol*, from *o*-iododimethylaniline and methyl dimethyl-*m*-aminobenzoate, crystallises in colourless plates, m. p. 151—152°.

2 : 3′ : 3″-*Hexamethyltriaminotriphenylcarbinol*, from *o*-iododimethylaniline and 3 : 3′-tetramethylaminobenzophenone, crystallises in prisms, m. p. 207—208°. G. Y.

Synthetical Ephedrines. ERNEST FOURNEAU (*J. Pharm. Chim.*, 1907, [vi], **25**, 593—602. Compare Abstr., 1905, i, 57; Schmidt, *ibid.*, 370).—The *methochloride* of benzyldimethylaminomethylcarbinol, derived from allylbenzene (*loc. cit.*), is a syrup; the *picrate* has m. p. 143°; the aurichloride and platinichloride are identical with the salts of Schmidt and Emde's quaternary base derived from cinnamyltrimethylamine hydrochloride (Abstr., 1906, i, 946). The base must have the constitution $OH\cdot CH(CH_2Ph)\cdot CH_2\cdot NMe_3\cdot OH$, and not that ascribed to it by these authors.

When heated with trimethylamine in benzene solution at 126°, the *chlorohydrin*, $OH\cdot CHPh\cdot CH_2\cdot CH_2Cl$, b. p. 142/°20 mm., prepared by Grignard's reaction from β-chloropropaldehyde, yields the quaternary *chloride*, $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot NMe_3Cl$, m. p. 210° (decomp.); the *aurichloride*, m. p. 155°, decomp. about 190°; the *platinichloride*, decomp. about 230°; the *base* decomposes when heated, yielding trimethylamine and an *alcohol*, b. p. 101—102°/21 mm., isomeric with cinnamyl alcohol.

γ-Methylamino-a-phenylpropyl alcohol, $OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot NHMe$, the fifth isomeride of ephedrine, is prepared by the action of methylamine on the chlorohydrin; it forms prisms, m. p. 70°, b. p. 170°/31 mm.; the *hydrochloride*, m. p. 130°: the *platinichloride*, m. p. 108—110°, decomposes when strongly heated.

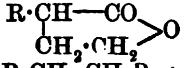
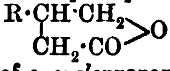
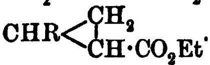
γ-Dimethylamino-a-phenylpropyl alcohol,

$$OH\cdot CHPh\cdot CH_2\cdot CH_2\cdot NMe_2,$$

crystallises in plates, m. p. 55°, b. p. 182°/64 mm.; the *hydrochloride*, m. p. 128°; the *aurichloride*, m. p. 120°, decomp. about 160°; the *platinichloride*, m. p. 130° (decomp.); the *methiodide*, $C_{12}H_{20}ONI$, forms needles, m. p. 118°. The *hydrochloride* of the *benzoyl* derivative,

$$C_{18}H_{21}O_2N,HCl,$$

crystallises in needles, m. p. 167°; the *hydrochloride* of the *cinnamoyl* derivative, m. p. 179°. G. Y.

Action of Some γ- and δ-Bromo-esters on Ethyl Cyanoacetate, Malonate, and Methylmalonate. GUSTAVE BLANC (*Compt. rend.*, 1907, **145**, 78—80).—By the successive action of phosphorus pentabromide and alcohol on the mixture of lactones, obtained (Abstr., 1905, i, 680, 681) by reduction of the acid anhydrides of the succinic or glutaric series, γ- or δ-bromo esters are obtained according as a γ- or δ-lactone is employd. These esters react readily with the sodium derivatives of ethyl cyanoacetate, malonate, or methylmalonate. Of the γ-bromo-esters, however, whilst those derived from lactones of the type  react normally according to the equation $CO_2Et\cdot CHR\cdot CH_2\cdot CH_2Br + CHNa(CO_2Et)_2 \longrightarrow CO_2Et\cdot CHR\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$, the ethers derived from lactones of the type  undergo a simple elimination of HBr with formation of a *cyclo*propanecarboxylic ester, thus: $CH_2Br\cdot CHR\cdot CH_2\cdot CO_2Et + CHNa(CO_2Et)_2 = NaBr + CH_2(CO_2Et)_2 +$ 

Thus condensation of ethyl γ-bromo-*aa*-dimethylbutyrate with one of the above sodium derivatives gives a cyanodicarboxylic or a tricarboxylic ester, but by condensing ethyl γ-bromo-ββ-dimethylbutyrate, *ethyl 2:2-dimethyl*cyclo*propanecarboxylate* is formed as a liquid, b. p. 90°/15 mm. The corresponding *acid* is an oil of a strong butyric odour, b. p. 100°/10 mm., and very stable towards potassium permanganate. It forms an *amide* crystallising in tablets, m. p. 177°. *Ethyl 2-iso*propylcyclo*propanecarboxylate*, similarly obtained from *iso*propylsuccinic acid, has b. p. 95—100°/10 mm. The corresponding *acid* is an oil with a butyric odour, b. p. 115°/15 mm., also stable towards permanganate. It gives an *amide*, forming tablets, m. p. 166—167°, and an *anilide*, crystallising in needles, m. p. 117°, and is probably identical with Ipatieff's acid (Abstr., 1902, i, 588).

When ethyl γ-bromo-ββ-dimethylvalerate is condensed with the sodium derivative of ethyl malonate or methylmalonate, besides the expected tricarboxylic ester, a quantity of an *ester*, b. p. 90°/8 mm., is formed, which gives an oily *acid*, b. p. 112—115°/12 mm., and an *amide*, m. p. 98°. This must be *ββ-dimethyl-Δ^{γ}-pentenoic acid*,

$$CH_2{:}CH{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

since it is oxidised by permanganate solution at −5° giving chiefly αα-dimethylsuccinic acid. E. H.

Affinity Constants of Tyrosine and Phenylalanine. Aristides Kanitz (*Pflüger's Archiv*, 1907, **118**, 539—546).—The basic and acidic dissociation constants for tyrosine and phenylalanine have been calculated from the degree of hydrolysis of their hydrochlorides and sodium salts by the method previously described (Abstr., 1906, ii, 603). As the compounds were only sparingly soluble, the degree of hydrolysis was determined by electrical conductivity methods.

The results obtained at 25° are for tyrosine:

First acid dissociation constant,	K_s,	4×10^{-9}
Second ,, ,, ,,	K_{ss},	4×10^{-10}
Basic ,, ,,	K_b,	$2{\cdot}6 \times 10^{-12}$

And for phenylalanine:

Acid dissociation constant,	K_s,	$2{\cdot}5 \times 10^{-9}$
Basic ,, ,,	K_b,	$1{\cdot}3 \times 10^{-12}$.

The acid dissociation constant of phenylaniline, calculated from the conductivities of solutions of phenylalanine itself, was high, but this value was reduced considerably when the compound had been repeatedly recrystallised. The salts of the specially purified compound gave the same results as the original salts. J. J. S.

Triphenylcarbinol: Action of Malonic and Cyanoacetic Acids. Robert Fosse (*Compt. rend.*, 1907, **145**, 196—198).—The action of malonic acid transforms triphenylcarbinol quantitatively into βββ-triphenylpropionic acid.

The action of cyanoacetic acid on triphenylcarbinol yields: (1) *α-cyano-βββ-triphenylpropionic acid* A, $CPh_3{\cdot}CH(CN){\cdot}CO_2H$, m. p. 155°, which is more soluble in ordinary solvents and less stable than the isomeric B-acid; on heating the acid, or an alcoholic solution of its sodium salt, it yields (2) *α-cyano-βββ-triphenylethane* A,

$$CPh_3{\cdot}CH_2{\cdot}CN,$$

m. p. 140°, which is also formed during the reaction between cyanoacetic acid and triphenylcarbinol; (3) *α-cyano-βββ-triphenylpropionic acid* B, m. p. 175° (decomp.), which on heating yields *α-cyano-βββ-triphenylethane* B, $C_{21}H_{17}N$, m. p. 211°.

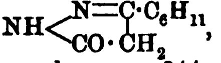
The nature of the isomerism of the two α cyano-βββ-triphenylpropionic acids and of their products of decarboxylation is unknown.

T. H. P.

Trimethylcoumarone. JOHANNES BOES (*Chem. Zentr.*, 1907, i, 1426; from *Apoth.-Zeit.*, **22**, 177).—A mixture of trimethylcoumarones has been isolated from a fraction of tar oil of b. p. 235—245°. The mixture had the characteristic odour of coumarone, did not solidify when cooled in ice and salt, and had b. p. 240°, D^{17} 1·0204, and n_D^{17} 1·5471; it decolorised bromine water in the cold, and gave a dark red coloration with concentrated sulphuric acid. The picrate, m. p. 105°, crystallised from alcohol in yellow needles, and was unstable. E. W. W.

Ethyl Hexahydrobenzoylacetate. ANDRÉ WAHL and A. MEYER (*Compt. rend.*, 1907, **145**, 192—194).—The authors give an account of their incomplete work, owing to the appearance of Zelinsky and Schwedoff's paper (this vol., i, 704).

Ethyl hexahydrobenzoylacetate, $C_6H_{11}\cdot CO\cdot CH_2\cdot CO_2Et$, prepared by condensing ethyl hexahydrobenzoate (1 mol.) and ethyl acetate (1 mol.) in presence of sodium (1 at.), has b. p. 140—143°/25 mm. The *methyl* ester, $C_6H_{11}\cdot CO\cdot CH_2\cdot CO_2Me$, has b. p. 140—141°/23 mm. These esters possess very persistent odours, which, when diluted, recall that of leather. They yield well crystallised copper salts, and have the properties of β-ketonic esters. Thus, with hydrazine hydrate in aqueous alcohol, they yield 3-cyclo*hexyl-5-pyrazolone*,



$$NH<\begin{matrix}N{=}C\cdot C_6H_{11}\\ CO\cdot CH_2\end{matrix},$$

which crystallises in white scales, m. p. 244—245°. T. H. P.

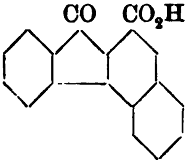
Complete Reduction of Ethyl Benzylacetoacetate. JULIUS TAFEL and HANS HAHL (*Ber.*, 1907, **40**, 3312—3318).—The reduction was carried out electrolytically with a lead cathode, using 7·5 grams of ester, 22·5 grams of 30% sulphuric acid, and 70 c.c. of 96% alcohol; the current employed was 2·4 amperes with a cathode surface of 20 cm^2. The nearly colourless reduction product, after washing with soda and drying, was treated with sodium hydrogen sulphite and ether, which removed *benzylacetoacetaldehyde*,

$$COMe\cdot CH(C_7H_7)\cdot CHO,$$

an intensely yellow oil, b. p. 76—81°, in the vacuum produced by liquid air; the *bisphenylhydrazone* is light yellow, m. p. 149°. The oil, freed from ether and water, was next fractionally distilled under 35 mm. pressure at 110°; the fraction consisted mainly of *β-benzylbutane*, $CH_2Me\cdot CH(C_7H_7)\cdot CH_3$, a colourless, mobile oil, b. p. 203—204°/750 mm. The residual oil was next distilled in the vacuum produced by liquid air and charcoal, and collected in three fractions: (1) up to 80°; (2) 80—125°; (3) 125—185°. Fraction (2) consisted largely of ethyl β-hydroxy-α-benzylbutyrate, and the second and third fractions both contained ethyl α-benzylbutyrate. The portion of (2), not hydrolysed, contained an alcohol (?) and *β-benzylbutyl ethyl ether*, $CH_3\cdot CH_2\cdot CH(C_7H_7)CH_2OEt$, b. p. 156—162°. W. R.

A Bordeaux-red Chrysoketonecarboxylic Acid and its Yellow Derivatives. A Contribution to the Theory of Colour. HANS STOBBE [and, in part, WILLY KEDING and FERDINAND GOLLÜCKE] (*Ber.*, 1907, **40**, 3383—3389).—Derivatives of chrysoketone or naphthafluorenone and of *iso*chrysoketone have been described previously by Bamberger and by Graebe and Gnehm (Abstr., 1905, i, 60).

An allo*chrysoketonecarboxylic acid* is formed when 1-phenylnaphthalene-2 : 3-dicarboxylic acid (this vol., i, 769) is treated with concentrated sulphuric acid for two days at the ordinary temperature and the product poured on to ice. It crystallises from benzene or cumene in bordeaux-red needles, m. p. 285—286° (decomp.). It is sparingly soluble in all solvents, and is stable towards oxidising agents. Chromic anhydride yields an acid which is neither benzoic nor *o*-benzoylbenzoic acid. It can be reduced with sodium amalgam at 100°.



The *sodium* salt, $C_{18}H_9O_3Na$, crystallises in orange-red needles, and the *potassium* salt in orange needles. The *ethyl* ester, $C_{20}H_{14}O_3$, obtained from the silver salt, crystallises from dilute alcohol in yellow needles, m. p. 187—188°. The *phenylhydrazone*, $C_{24}H_{16}O_2N_2$, also forms yellow needles, m. p. 241°. The absorption spectra of the acid and its derivatives have been examined in solution. All yield a continuous absorption band, but that of the acid extends further towards the red end of the spectrum.

The difference in colour between the acid and its salts does not appear to be due to any molecular rearrangement during the salt formation, as would be required by Hantzsch's theory. J. J. S.

Synthesis of Salicyluric Acid. SAMUEL BONDI (*Zeitsch. physiol. Chem.*, 1907, **52**, 170—176).—Salicyluric acid has been synthesised by the action of glycine on an alkaline solution of the azoimide of salicylic acid,

$$OH\cdot C_6H_4\cdot CO\cdot N_3 + NH_2\cdot CH_2\cdot CO_2H + 2NaOH = OH\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2Na + NaN_3 + 2H_2O.$$

A by-product formed in the reaction is sparingly soluble in alcohol and has m. p. 230—231°. The analyses of salicyluric acid invariably gave too high a percentage of carbon.

Salicylic acid hydrazide, $OH\cdot C_6H_4\cdot CO\cdot NH\cdot NH_2$, obtained by heating ethyl salicylate and hydrazine hydrate for two and a half hours on the water-bath, has m. p. 147° (Struve and Radenhausen, Abstr., 1896, i, 35, give 145°). Sodium nitrite reacts with a nitric acid solution of the hydrazide, yielding the azoimide, $OH\cdot C_6H_4\cdot CO\cdot N_3$, in the form of crystalline plates with a pungent odour. J. J. S.

Ester- and Amide-acids of Phenylsuccinic Acid. RICHARD ANSCHÜTZ (*Annalen*, 1907, **354**, 117—151).—In conjunction with the investigation of the partial esterification of itaconic and mesaconic acids and the partial hydrolysis of their methyl and ethyl esters (Abstr., 1898, i, 128; this vol., i, 468), the same reactions have been studied with *aa*-dimethylsuccinic (Güttes, *Diss.*, *Bonn*, 1901; compare Blaise, Abstr., 1898, i, 560) and phenylsuccinic (Hahn, *Diss.*, *Bonn*, 1902) acids in order to compare the behaviour of an asymmetrical saturated acid with that of asymmetrical unsaturated acids, and to determine the influence of the negative phenyl group on the activity of the carboxyl attached to the same carbon atom. At the same time, the manner in which the anhydrides of these acids combine with alcohols, ammonia, and substituted ammonias has been studied.

In the present paper, the author describes the preparation of phenylsuccin-*a*-amic acid and hydrogen β-methyl phenylsuccinate from β-cyano-β-phenylpropionic acid, the formation of the hydrogen methyl phenylsuccinates and of the corresponding acid-chlorides from phenylsuccinic acid, the isomerism of the phenylsuccin-amic, -anilic, -*p*-toluidic, and -piperidic acids, and the synthesis of β-benzoyl-α-phenyl- and β-benzoyl-β-phenyl-propionic acids from phenylsuccinic acid.

The hydrogen methyl phenylsuccinates were prepared by Wegscheider and Hecht (Abstr., 1903, i, 760), who considered the ester, m. p. 102°, obtained by partial hydrolysis of methyl phenylsuccinate, to be the α- and that, m. p. 92°, formed by partial esterification to be the β-methyl ester. These assumptions are shown now to have been correct, since on conversion into the corresponding ester-chloride and treatment with benzene and aluminium chloride, the β-methyl ester, $CO_2H\cdot CHPh\cdot CH_2\cdot CO_2Me$, yields methyl β-benzoyl-β-phenylpropionate, $COPh\cdot CHPh\cdot CH_2\cdot CO_2Me$, whilst the α-methyl ester,

$$CO_2Me\cdot CHPh\cdot CH_2\cdot CO_2H,$$

forms methyl β-benzoyl-α-phenylpropionate, $CO_2Me\cdot CHPh\cdot CH_2\cdot COPh$. Moreover, β-cyano-β-phenylpropionic acid on partial hydrolysis yields phenylsuccin-α-amic acid, but on esterification and subsequent partial hydrolysis forms hydrogen β-methyl phenylsuccinate:

$$\begin{tikzcd}
CN\cdot CHPh\cdot CH_2\cdot CO_2H \arrow[r] \arrow[d] & NH_2\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2H & \\
CN\cdot CHPh\cdot CH_2\cdot CO_2Me \arrow[r] & NH_2\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2Me \arrow[r] & CO_2H\cdot CHPh\cdot CH_2\cdot CO_2Me.
\end{tikzcd}$$

The action of methyl alcohol on phenylsuccinic anhydrides leads to the formation of a mixture containing about 25% of the more feebly acid hydrogen α-methyl and about 75% of the more strongly acid hydrogen β-methyl phenylsuccinates. The mixture of methyl amates, formed from this by way of the acid-chlorides, is readily separated in consequence of the difference in solubility of the isomerides in ether. The -β-amic, -β-anilic, -*p*-toluidic, and -β-piperidic acids are obtained directly and without admixture of the α-isomerides by the action of ammonia or substituted ammonias on phenylsuccinic anhydride, the basic group combining with the carbonyl of the more feebly acid carboxyl.

Conversion of β-Cyano-β-phenylpropionic Acid and its Methyl Ester into Phenylsuccin-α-amic Acid and Hydrogen β-Methyl Phenylsuccinate.—[With PAUL WALTER.]—*Phenylsuccin-α-amic acid*, $C_{10}H_{11}O_3N$, prepared by the action of concentrated sulphuric acid on α-cyano-α-phenylpropionic acid (Bredt and Kallen, Abstr., 1897, i, 154) at the ordinary temperature, crystallises from water in small plates, m. p. 158—159°; the *silver* salt, $C_{10}H_{10}O_3NAg$, is a white powder. The *methyl* ester, $CN\cdot CHPh\cdot CH_2\cdot CO_2Me$, prepared in the same manner as the ethyl ester (Bredt and Kallen, *loc. cit.*), crystallises in needles or prisms, m. p. 55°, b. p. 155—159°/10 mm., and when treated with concentrated sulphuric acid at the ordinary temperature yields *β-methyl phenylsuccin-α-amate*, $NH_2\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2Me$, m. p. 145°, which is only sparingly soluble in ether, and is converted by sulphuric and nitrous acids into hydrogen β-methyl phenylsuccinate, m. p. 92°.

Formation of the Hydrogen Methyl Phenylsuccinates and their Chlorides.—[With Carl Hahn and Paul Walter.]—Methyl phenylsuccinate (Wegscheider and Hecht, *loc. cit.*), m. p. 57—58°, b. p. 160—162°/12 mm. Phenylsuccinic anhydride, b. p. 191—192°/12 mm.

Phenylsuccinyl dichloride, $COCl\cdot CHPh\cdot CH_2\cdot COCl$, is obtained as a colourless liquid, b. p. 150—151°/12 mm., and has an irritating odour.

On hydrolysis with methyl alcoholic potash at the ordinary temperature, 12·7 grams of methyl phenylsuccinate gave 6·3 grams of the α-monomethyl ester and 3·3 grams of the acid, 2·6 grams remaining unchanged; in another experiment, 8·8 grams of the dimethyl ester gave 6·0 grams of the α-methyl ester and 0·2 gram of acid, 1·2 grams being unchanged.

The *methyl phenylsuccinyl chlorides*, $CO_2Me\cdot CHPh\cdot CH_2\cdot COCl$ and $COCl\cdot CHPh\cdot CH_2\cdot CO_2Me$, formed by heating the monomethyl esters, or a mixture of these, with phosphorus trichloride at 60—70°, are obtained as colourless oils which could not be purified, as they decompose on distillation in a vacuum.

*The Isomeric Phenylsuccin-amic, -anilic, -*p*-toluidic, and -piperidic Acids.*—[With Carl Hahn and Paul Walter.]—*Phenylsuccin-β-amic acid*, $CO_2H\cdot CHPh\cdot CH_2\cdot CO\cdot NH_2$, m. p. 144—145°, prepared by the action of anhydrous ammonia on phenylsuccinic anhydride in ethereal solution, crystallises from water; the white *silver* salt, $C_{10}H_{10}O_3NAg$, darkens on exposure to light; the *methyl* ester, $C_{11}H_{13}O_3N$, m. p. 119°, formed by the action of methyl iodide on the silver salt or of ammonia on the ester-chloride, is readily soluble in ether, and yields hydrogen α-methyl phenylsuccinate when treated with nitrous acid.

The methyl phenylsuccinanilates are prepared by the action of aniline on the ester-chlorides, and, when formed together from a mixture of these, can be partially separated by crystallisation from ether, the β-methyl anilate being the more readily soluble. On careful hydrolysis, the esters yield the anilic acids.

Phenylsuccin-β-anilic acid, m. p. 169—170°, was prepared by Hann and Lapworth (Trans., 1904, **85**, 1367) by the action of aniline on phenylsuccinic anhydride, and considered by these authors to be the α-anilic acid; the *silver* salt, $C_{16}H_{14}O_3NAg$, was analysed; the *methyl* ester, $CO_2Me\cdot CHPh\cdot CH_2\cdot CO\cdot NHPh$, crystallises in white needles, m. p. 149°. The *α-anilic acid*, $NHPh\cdot CO\cdot CHPh\cdot CH_2\cdot CO_2H$, has m. p. 175°; the *methyl* ester, $C_{17}H_{17}O_3N$, m. p. 96°. A mixture of the two anilic acids has m. p. 159—160°. When heated with acetyl chloride, both anilic acids yield phenylsuccinanil (Hann and Lapworth, *loc. cit.*).

Phenylsuccindianilide, $NHPh\cdot CO\cdot CHPh\cdot CH_2\cdot CO\cdot NHPh$, m. p. 222°, is formed by shaking phenylsuccinyl dichloride with aniline in ethereal solution; if the reacting substances are present in molecular proportions, half of the dichloride remains unchanged.

The *p*-toluidic and piperidic acids are formed and behave in the same manner as the anilic acids.

*Phenylsuccin-β-*p*-toluidic acid*, $CO_2H\cdot CHPh\cdot CH_2\cdot CO\cdot NH\cdot C_7H_7$, m. p. 168—169°; the *silver* salt, $C_{17}H_{16}O_3NAg$, was analysed; the *methyl* ester, $C_{18}H_{19}O_3N$, m. p. 118°. The *α-*p*-toluidic acid*, m. p.

175°; the *methyl* ester, m. p. 118°. A mixture of the two methyl esters has m. p. about 105°. When heated with acetyl chloride, the *p*-toluidic acids form phenylsuccino-*p*-tolil (Hann and Lapworth, *loc. cit.*).

Phenylsuccin-β-piperidic acid, $CO_2H\cdot CHPh\cdot CH_2\cdot CO\cdot C_5NH_{10}$, crystallises in white needles, m. p. 95°; the *silver* salt was analysed; the ester, $C_{16}H_{21}O_3N$, forms monoclinic crystals, m. p. 109°. The *α-piperidic acid*, $C_{15}H_{19}O_3N$, m. p. 165°; the *methyl* ester, m. p. 97°. A mixture of the methyl esters has m. p. 79—80°.

Synthesis of Desylacetic and Phenylphenacylacetic Acids from Phenylsuccinic Acid.—[With PAUL WALTER.]—*Methyl β-benzoyl-β-phenylpropionate*, $C_{17}H_{16}O_3$, m. p. 49°, is prepared by the action of β-methyl phenylsuccinyl chloride on benzene in presence of aluminium chloride, and on hydrolysis with potassium hydroxide yields β-benzoyl-β-phenylpropionic (desylacetic) acid (Meyer and Oelkers, Abstr., 1888, 704), which is formed also by the action of phenylsuccinic anhydride on benzene in presence of aluminium chloride.

The methyl ester, obtained by the action of α-methyl succinyl chloride on benzene in presence of aluminium chloride, is identical with methyl β-benzoyl-α-phenylpropionate prepared from benzylideneacetophenone (Anschütz and Montfort, Abstr., 1895, i, 179).

G. Y.

A Product of the Action of Light on Diphenylfulgide and the Polymerisation of Phenylpropiolic Acid.

HANS STOBBE [and, in part, WILLY KEDING, PHOKION NAÓUM, and VICTOR VON VIGIER] (*Ber.*, 1907, **40**, 3372—3382).—The colourless anhydride (Abstr., 1904, i, 589), obtained by exposing a benzene solution of diphenylfulgide (dibenzylidenesuccinic anhydride) to sunlight, is identical with the anhydride obtained by the action of acetic anhydride or phosphoryl chloride on phenylpropiolic acid (Michael and Bucher, Abstr., 1898, i, 256; Lanser, *ibid.*, 1899, i, 916; Manthey, *ibid.*, 1901, i, 31; Lanser and Halvorsen, *ibid.*, 1902, i, 458; compare also Ruhemann and Merriman, Trans., 1905, **87**, 1389). This anhydride is shown to have the constitution attributed to it by Michael and Bucher, namely, 1-phenylnaphthalene-2:3-dicarboxylic anhydride, and not that suggested by Lanser, namely, diphenyl*cyclo*butadienedicarboxylic anhydride. When oxidised with chromic anhydride in acetic acid solution, it yields *o*-benzoylbenzoic acid, a reaction which is not compatable with Lanser's formula.

Oxidation with alkaline permanganate gives rise to resinous acids, oxalic and benzoic acids, and in one experiment to a soluble acid, m. p. 200°, and in another to benzaldehyde. Diphenyltetracarboxylic acid, phthalic acid, and *o*-benzoylbenzoic acid could not be detected (compare Michael and Bucher, *loc. cit.*). Reduction with sodium amalgam converts the 1-phenylnaphthalene-2:3-dicarboxylic acid into Michael and Bucher's 1:2:3:4-tetrahydro-derivative, which melts at 204° and decomposes at 207°. Chromic acid oxidises this reduction product also to *o*-benzoylbenzoic acid. The anhydride of the tetrahydro-acid has m. p. 155°.

β-Truxillic acid, which is isomeric with the phenylnaphthalene-dicarboxylic acid, is less readily oxidised than the naphthalene acid and yields as final product benzil.

The lactone, $C_{18}H_{12}O_2$, described by Michael and Bucher, could not be obtained by the action of zinc dust and acetic anhydride on the anhydride; the only product isolated was the tetrahydro-anhydride.

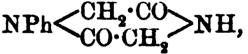
J. J. S.

Isomeric Esters of Carbethoxyglycylglycine. HERMANN LEUCHS and WILHELM MANASSE (*Ber.*, 1907, 40, 3235—3249).—Ethyl carbethoxyglycylglycine presents two points of interest; it exists in two apparently structurally identical forms, which, however, exhibit marked differences in chemical and physical properties, and, secondly, it yields by hydrolysis glycylglycine-*N*-carboxylic acid, which has an unusual degree of stability (Fischer, Abstr., 1902, 350; 1903, 465). The authors claim that the acid obtained by hydrolysis cannot be glycylglycine-*N*-carboxylic acid, which has been synthesised by Siegfried (Abstr., 1906, i, 144) and Leuchs (*ibid.*, i, 236); moreover, they assert that the isomerism of the ester is an example of lactam and lactim formation. The ester and its derivatives having the lactam formula $CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$ are termed members of the α-series, whilst members of the β-series have the lactim formula $CO_2Et\cdot NH\cdot CH_2\cdot C(OH):N\cdot CH_2\cdot CO_2Et$. The ester of the α-series undergoes transformation during hydrolysis, and yields the dicarboxylic acid of the β-series.

To obtain confirmation of this view, *ethyl carbethoxyglycyl*-N-*phenylglycine*, $CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot CO_2Et$, m. p. 58—59°, and *ethyl carbethoxy*-N-*phenylglycylglycine*, $CO_2Et\cdot NPh\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, have been examined. The former, which is prepared from carbethoxyglycyl chloride and ethyl *N*-phenylglycine in dry ether at 0°, is incapable of undergoing transformation into the lactim, and consequently yields by hydrolysis the crystalline peptide, *glycyl*-1-*phenylglycine*,

$$NH_2\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot CO_2H,$$

which when heated passed into 1-*phenyldiketopiperazine*,



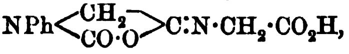
$$NPh\mathord{<}\begin{matrix}CH_2\cdot CO\\ CO\cdot CH_2\end{matrix}\mathord{>}NH,$$

m. p. 251° (corr.); this is also obtained from chloroacetylphenylglycine and ammonium hydroxide at 100°.

Ethyl carbethoxy-N-*phenylglycylglycine* (α-series), m. p. 62—63°, is prepared from carbethoxy-*N*-phenylglycyl chloride and ethyl glycine in anhydrous ether. By hydrolysis with normal sodium hydroxide, it yields N-*phenylglycylglycine*-N-*carboxylic acid*,

$$CO_2H\cdot NPh\cdot CH_2\cdot C(OH):N\cdot CH_2\cdot CO_2H,$$

which does not lose carbon dioxide, and is the analogue of Fischer's so-called glycylglycine-*N*-carboxylic acid; it differs from the latter in the ease with which it forms the *lactone*,

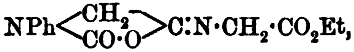


$$NPh\mathord{<}\begin{matrix}CH_2\\ CO\cdot O\end{matrix}\mathord{>}C:N\cdot CH_2\cdot CO_2H,$$

m. p. 255—256° (corr.), the change occurring slowly at the ordinary temperature, instantly on heating, or in the presence of hydrochloric acid. A similar anhydride formation is observed with the derivatives of *N*-phenylglycylglycine-*N*-carboxylic acid; thus, when ethyl carbethoxy-*N*-phenylglycylglycine (α-series) is treated with cold alcoholic ammonia, *carbethoxy*-N-*phenylglycylglycinamide*,

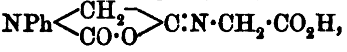
$$CO_2Et\cdot NPh\cdot CH_2\cdot C(OH):N\cdot CH_2\cdot CO\cdot NH_2,$$

is formed, which has m. p. 137° (corr.), and at 220° evolves alcohol, forming the *lactone*, $NPh{<}\begin{matrix}CH_2\\CO\cdot O\end{matrix}{>}C:N\cdot CH_2\cdot CO\cdot NH_2$, m. p. 305° (corr.), which is produced directly from the original ester and methyl alcoholic ammonia at 100°, and also from the *ester*,



$$NPh{<}\begin{matrix}CH_2\\CO\cdot O\end{matrix}{>}C:N\cdot CH_2\cdot CO_2Et,$$

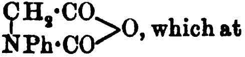
m. p. 155° (corr.), which is prepared by esterifying the corresponding lactone-acid or its crude parent dicarboxylic acid.

The normal *silver* salt of the dicarboxylic acid, $C_{11}H_{10}O_5N_2Ag_2$, is obtained by heating the lactone acid,  $NPh{<}\begin{matrix}CH_2\\CO\cdot O\end{matrix}{>}C:N\cdot CH_2\cdot CO_2H$, with sodium hydroxide on the water-bath, neutralising the solution with nitric acid, and adding silver nitrate, whereby the silver salt is precipitated. It is a voluminous, white powder, which quickly darkens in the light, and is decomposed by boiling water, silver oxide being precipitated with the formation of the *silver* salt of the lactone acid, $C_{11}H_9O_4N_2Ag$.

Ethyl carbethoxy-N-*phenylglycylglycine* (β-series),

$$CO_2Et\cdot NPh\cdot CH_2\cdot C(OH):N\cdot CH_2\cdot CO_2Et,$$

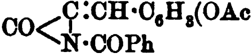
m. p. 107° (corr.), prepared from the first-mentioned silver salt and ethyl iodide, differs from the isomeric ester of the α-series in its tendency to form a lactone; by heating at 220° or with alcoholic hydrogen chloride, it loses alcohol and yields the lactone ester, m. p. 153—154°, described previously.

The *carbethoxy*-N-*phenylglycyl chloride*, $CO_2Et\cdot NPh\cdot CH_2\cdot COCl$, used in the preparation of the ester of the α-series, is obtained from carbethoxy-*N*-phenylglycine (Lumière and Barbier, Abstr., 1906, i, 245) and excess of thionyl chloride in a freezing mixture. If only the calculated quantity of thionyl chloride is employed, the main product of the reaction is N-*carboxy*-N-*phenylglycine anhydride*,  $\begin{matrix}CH_2\cdot CO\\ | \\ NPh\cdot CO\end{matrix}{>}O$, which at its m. p. 142° (corr.), loses carbon dioxide, forming an amorphous *substance*, $(NPh\cdot CH_2\cdot CO)_x$, and is converted by alcoholic ammonia into *N*-phenylglycinamide. C. S.

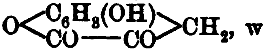
Synthesis of Alcaptonic Acids. OTTO NEUBAUER and LEOPOLD FLATOW (*Zeitsch. physiol. Chem.*, 1907, 52, 375—398. Compare Kirk, Abstr., 1890, 188; Wolkow and Baumann, Abstr., 1891, 1128; Baumann and Fränkel, *Zeitsch. physiol. Chem.*, 1894, 20, 210; Huppert, Abstr., 1897, ii, 576; 1899, ii, 706).—Synthetical α-2:5-dihydroxyphenylpropionic acid is not identical with Kirk's uroleucic acid. The synthesis consists in condensing gentisaldehyde (2:5-dihydroxybenzaldehyde) with hippuric acid, hydrolysing the condensation product with concentrated sodium hydroxide to α-2:5-trihydroxycinnamic acid or the corresponding keto-form, 2:5-dihydroxyphenylpyruvic acid, and reducing this keto-acid with sodium amalgam and water.

Only a small yield of gentisaldehyde is obtained by condensing quinol with chloroform in the presence of potassium hydroxide, but an excellent yield may be obtained by oxidising salicylaldehyde with potassium persulphate in the presence of sodium hydroxide, the aldehyde group remaining intact.

The condensation product obtained from hippuric acid and gentisaldehyde in the presence of acetic anhydride and sodium acetate is the *inner* anhydride of *a-benzoylamino-*2 : 5*-diacetoxycinnamic acid,*



$CO<\begin{matrix}C{:}CH\cdot C_6H_3(OAc)_2\\ N\cdot COPh\end{matrix}$, which forms a yellow, crystalline powder consisting of minute prisms, m. p. 190°. When hydrolysed with 40% sodium hydroxide solution in the absence of air, it yields ammonia, benzoic acid, and the *anhydride* of 2 : 5-dihydroxyphenylpyruvic acid,



$O<\begin{matrix}C_6H_3(OH)\\ CO—CO\end{matrix}>CH_2$, which crystallises in plates containing water of crystallisation, or from boiling water in anhydrous needles, m. p. above 200°. It gives a characteristic green coloration with ferric chloride, especially in alcoholic solution; its alkaline solutions turn brown on exposure to the air, and reduce warm ammoniacal silver nitrate solution. The corresponding *acid,* $C_6H_3(OH)_2\cdot CH_2\cdot CO\cdot CO_2H$, is obtained when a solution of the sodium salt is acidified, but tends to reform the anhydride, especially in faintly acid solution. With ferric chloride in 50% alcoholic solution, it yields a reddish-violet coloration, which changes to an evanescent green colour.

a : 2 : 5*-Trihydroxyphenylpropionic acid,*

$$C_6H_3(OH)_2\cdot CH_2\cdot CH(OH)\cdot CO_2H,$$

is somewhat difficult to obtain in a crystalline state, it forms well developed, colourless prisms containing $1H_2O$, and has m. p. 87°.

2 : 5*-Dihydroxycinnamic acid,* $C_6H_3(OH)_2\cdot CH{:}CH\cdot CO_2H$, obtained by oxidising a 5% solution of *o*-coumaric acid in excess of sodium hydroxide with a 10% solution of potassium persulphate and hydrolysing the alkyl sulphate thus formed with concentrated hydrochloric acid, has m. p. 207° (decomp.). The *anhydride* of 2 : 5-dihydroxyphenylpropionic acid, $C_9H_8O_3$, obtained in a similar manner from *o*-hydrocoumaric acid, has m. p. 163°. 2 : 5*-Dihydroxyphenylglyoxylic acid,* $C_6H_3(OH)_2\cdot CO\cdot CO_2H$, obtained from *o*-hydroxyphenylglyoxylic acid, crystallises from a mixture of ether, benzene, and light petroleum in yellow needles. When dried over sulphuric acid, or heated at 40°, or when exposed to sunlight, it is transformed into a red modification, m. p. 141°, which can be reconverted into the yellow compound by moistening with water. When reduced with sodium amalgam and water, the glyoxylic acid yields 2 : 5*-dihydroxymandelic acid,*

$$C_6H_3(OH)_2\cdot CH(OH)\cdot CO_2H,$$

m. p. 143° (decomp.), insoluble in benzene or light petroleum; but when reduced with excess of hydriodic acid, it yields homogentisic acid (2 : 5-dihydroxyphenylacetic acid).

The following properties are characteristic of all these alcaptonic acids. 1. Their alkaline solutions darken on exposure to air. 2. They reduce Fehling's solution and also cold ammoniacal silver nitrate. 3. They produce a black coloration with osmic acid.

4. They do not yield precipitates with bromine water or with dilute lead acetate solution. J. J. S.

Formation of Chains. LXX. Nitrophenoxymalonic Esters. Carl A. Bischoff (*Ber.*, 1907, 40, 3134—3150. Compare Abstr., 1900, i, 442; this vol., i, 35).—Sodium *o*-, *m*-, and *p*-nitrophenoxides react with malonic esters in benzene or xylene solution, according to the equation: $ONa{\cdot}C_6H_4{\cdot}NO_2 + CXBr(CO_2Y)_2 =$
$NaBr + NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CX(CO_2Y)_2$, (X = H, Me, Et; Y = Me, Et). A pure product has been obtained from sixteen of the eighteen possible reactions. The products of the action of sodium *o*-nitrophenoxide on methyl and ethyl bromoethylmalonate could not be isolated. In some cases, the potassium nitrophenoxides are employed in benzene or toluene solution. A table is given showing the extent, estimated by titration of the sodium bromide formed, to which the reactions take place in boiling benzene and boiling xylene, under varying conditions as to time and concentration of the ester. The reaction takes place most easily with the *m*-nitrophenoxide and X = Me, least so with the *o*-nitrophenoxide and X = Et. With X = Et and *o*- or *p*-nitrophenoxide, the difference of the reaction temperature in 0·07*N*-benzene or 0·35*N*-xylene solution has little influence on the yields, but with X = Me and *o*-nitrophenoxide, the reaction takes place to the extent of 17% in xylene, but not at all in benzene, whilst with other combinations the influence of the solvent is more marked, and with *m*-nitrophenoxide and X = H, the yields in both solvents approach the theoretical. In most cases, the group Y has little or no influence on the reaction, but with *p*-nitrophenoxide and X = Me, Y = Me gives an 83%, but Y = Et only a 54% yield, whilst with X = Et, Y = Me gives a 71%, but Y = Et a 45% yield.

Methyl bromomethylmalonate, $C_6H_9O_4Br$, is a colourless oil, b. p. 101°/16 mm.

Methyl ethylmalonate, $C_7H_{12}O_4$, is a colourless oil, b. p. 178—179°, D_4^4 1·104 (corr.). The *bromo*-derivative, $C_7H_{11}O_4Br$, is a colourless oil, b. p. 111°/16 mm.

Ethyl bromoethylmalonate, b. p. 115—119°/16 mm. (125°/10 mm.: Ruhemann, Abstr., 1894, i, 14).

The following nitrophenoxymalonic esters, $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CX(CO_2Y)_2$, are described.

o-Nitro-derivatives: X = H, Y = Me, colourless needles, m. p. 123°; X = H, Y = Et, colourless needles, m. p. 116—118°; X = Me, Y = Me, yellow plates, m. p. 75—76° X = Me, Y = Et, yellowish-brown plates, m. p. 118—119°.

m-Nitro-derivatives: X = H, Y = Me, yellow leaflets, m. p. 100°; X = H, Y = Et, colourless leaflets, m. p. 78°; X = Me, Y = Me, yellow prisms, m. p. 94°; X = Me, Y = Et, a viscid oil, b. p. 210—212°/16 mm.; X = Et, Y = Me, yellow plates, m. p. 95—96°, b. p. 234—236°/49 mm.; X = Et, Y = Et, a viscid, yellow oil, b. p. 218°/25 mm.

p-Nitro-derivatives: X = H, Y = Me, yellow, monoclinic prisms, m. p. 101°, b. p. 221—222°/15 mm. (slight decomp.), forms a brownish-yellow, amorphous *sodium* derivative, $C_{11}H_{10}O_7NNa$; X = Pr, Y = Me, white needles or plates, m. p. 112°; X = H, Y = H, white needles, decomp. 168—170°, forming *p*-nitrophenoxyacetic acid. On treatment with red phosphorus, bromine, and methyl alcohol, this acid yields a *substance*, m. p. 89—90°, which does not form potassium bromide when boiled with alcoholic potassium hydroxide. Ethyl *p*-nitrophenoxyacetate, b. p. 203—206°/15 mm. (Kym, Abstr., 1897, i, 283), does not form a bromo-derivative at 150°. X = H, Y = Et, white needles, m. p. 86°, b. p. 241—242°/15 mm. (slight decomp.), forms a brownish-yellow *sodium* derivative, $C_{13}H_{14}O_7NNa$, and a *bromo*-derivative,

$$C_{13}H_{14}O_7NBr,$$

plates, m. p. 95°.. X = Me, Y = Me, colourless needles, m. p. 174°; X = Me, Y = Et, needles, m. p. 141—142°; X = Et, Y = Me, white needles, m. p. 173—174°; X = Et, Y = Et, colourless needles, m. p. 142°.

G. Y.

Formation of Chains. LXXI. Bisnitrophenoxymalonic Esters, Bisnitrophenoxyethanetetracarboxylic Esters, and an Unexpected Case of Isomerism with the Former. CARL A. BISCHOFF (*Ber.*, 1907, 40, 3150—3177. Compare Abstr., 1897, i, 267; Conrad and Brückner, Abstr., 1892, 39; Curtiss, Abstr., 1897, i, 556).—The sodium nitrophenoxides react with methyl and ethyl dibromomalonates in boiling xylene solution, forming bisnitrophenoxymalonic esters, $C(O\cdot C_6H_4\cdot NO_2)_2(CO_2R)_2$. The manner in which the reaction is influenced by the position of the nitro-group, by the group R, and by the concentration of the ester is shown by the following quantitative results. The percentages are the amounts of sodium bromide formed; the concentrations are those of the esters in the xylene.

Sodium *o*-nitrophenoxide: R = Me, 0·35*N*, 25%; 0·62*N*, 32%; 2*N*, 92%; R = Et, 0·35*N*, 31%; 2*N*, 87%. *m*-Nitrophenoxide: R = Me, 0·35*N*, 91%; R = Et, 0·35*N*, 93%. *p*-Nitrophenoxide: R = Me, 0·35*N*, 88%; R = Et, 0·35*N*, 86%.

The six methyl and ethyl bisnitrophenoxymalonates have been isolated and are described. The esters of the para-series are obtained in two modifications; that melting at the higher temperature is distinguished as the A-, the other as the B-, modification. Bis-*p*-nitrophenoxymalonic acid is obtained in only one modification, which, on esterification with alcohol and hydrochloric acid, yields a mixture of the two isomeric esters. The constitutions of these are discussed and possible formulæ suggested.

Bisnitrophenoxyethanetetracarboxylic esters,

$$NO_2\cdot C_6H_4\cdot O\cdot C(CO_2R)_2\cdot C(CO_2R)_2\cdot O\cdot C_6H_4\cdot NO_2,$$

are formed in small amounts by the action of bromonitrophenoxymalonic esters, $NO_2\cdot C_6H_4\cdot O\cdot CBr(CO_2R)_2$, on sodionitrophenoxymalonic esters, $NO_2\cdot C_6H_4\cdot O\cdot CNa(CO_2R)_2$, in boiling xylene, but not in alcoholic solution; the main product of the reaction in either solvent is the bisnitrophenoxymalonic ester, which is formed also by the action of iodine on the sodionitrophenoxymalonic ester. Small amounts of nitrophenoxymalonic and bisnitrophenoxyacetic esters are also formed.

Attempts to prepare methyl bis-*p*-nitrobenzylethanetetracarboxylate by the action of *p*-nitrobenzyl chloride on methyl disodioethanetetracarboxylate led to the formation of methyl *p*-nitrobenzylethanetetracarboxylate,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot C(CO_2Me)_2\cdot CH(CO_2Me)_2,$$

together with 4 : 4′-dinitrostilbene and an oil which may be *p*-nitrobenzyl methyl ether.

Methyl bis-o-*nitrophenoxymalonate*, $C_{17}H_{14}O_{10}N_2$, yellow needles, m. p. 131°. The *ethyl* ester, $C_{19}H_{18}O_{10}N_2$, yellow leaflets, m. p. 119°.

Methyl bis-m-*nitrophenoxymalonate*, yellow prisms, m. p. 100°. The *ethyl* ester, yellowish-white prisms, m. p. 72°. These two esters decompose when distilled in a vacuum.

Methyl chlorobromomalonate, $C_5H_6O_4ClBr$, colourless leaflets, m. p. 40—42°.

Methyl bis-p-*nitrophenoxymalonate A* crystallises in colourless needles, m. p. 175°. The *B-ester* crystallises in white needles, m. p. 136°, is more readily soluble than the A-ester in organic solvents, and decomposes at 190°/20 mm. When hydrolysed with alcoholic sodium hydroxide in acetone solution at 25°, the two modifications have approximately the same velocity constant for the first half of the reaction. Both esters are unimolecular. On treatment with sodium methoxide in acetone solution, the A-ester is partially hydrolysed and partially transformed into the B-ester. The action of sodium on methyl bromo-*p*-nitrophenoxymalonate in alcoholic solution leads to the formation of the A-ester, m. p. 175°, together with *methyl* p-*nitrophenoxymethoxymalonate*, $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}C(CO_2Me)_2{\cdot}OMe$, which crystallises in white leaflets, m. p. 65—67°, b. p. 188°/12 mm.

Ethyl bis-p-*nitrophenoxymalonate A*, $C_{19}H_{18}O_{10}N_2$, hexagonal plates or needles, m. p. 144°. The *B-ester*, yellowish-white needles, m. p. 119°, more readily soluble than the A-ester. The A-ester is obtained by the action of sodium *p*-nitrophenoxide on ethyl dichloromalonate, chlorobromomalonate, dibromomalonate, or bromo-*p*-nitrophenoxymalonate, or of ethyl sodio-*p*-nitrophenoxymalonate on ethyl bromo-*p*-nitrophenoxymalonate in xylene solution. A mixture of the A- and B-esters is obtained by the action of hydrogen chloride on bis-*p*-nitrophenoxymalonic acid in alcoholic solution, or of ethyl sodio-*p*-nitro phenoxymalonate on ethyl bromo-*p*-nitrophenoxymalonate in alcoholic solution, or of ethereal iodine on ethyl sodio-*p*-nitrophenoxymalonate in alcohol.

Bis-p-*nitrophenoxymalonic acid*, $C_{15}H_{10}O_{10}N_2$, forms rhombohedric crystals and loses carbon dioxide at 127—129°, m. p. 189°; the *sodium* salt, $C_{15}H_8O_{10}N_2Na_2$, is obtained as a white, voluminous precipitate, and has the conductivity $\lambda_{1024} - \lambda_{32} = 32$, whereas disodium salts of dibasic organic acids have usually the value 15 – 20. The *silver* salt forms the A-methyl ester when boiled with methyl iodide and benzene.

Bis-p-*nitrophenoxyacetic acid*, $CH(O{\cdot}C_6H_4{\cdot}NO_2)_2{\cdot}CO_2H$, formed from the malonic acid by heating at 170° or by prolonged boiling with water, crystallises in white needles, m. p. 188—189°, and when heated at 195—200° decomposes, forming chiefly *p*-nitrophenol. The *methyl* ester, $C_{15}H_{12}O_8N_2$, formed by the action of hydrogen chloride and methyl alcohol on the acid, or of iodine or methyl bromo-*p*-nitrophenoxymalonate on methyl sodio-*p*-nitrophenoxymalonate, or of methyl iodide on potassium *p*-nitrophenoxymalonate in alcoholic solution, or in small amount by the action of methyl iodide on the sodiomalonate in xylene, crystallises in prismatic needles, m. p. 146°. The *ethyl* ester, $C_{16}H_{14}O_8N_2$, prepared by the action of hydrogen chloride on the acid in alcoholic solution, crystallises in white needles, m. p. 137°.

Ethanetetracarboxylic esters are readily identified by conversion into the *tetra-anilide*, $C_2(CO{\cdot}NHPh)_4$, which crystallises in microscopic prisms or needles, m. p. 270° (decomp.).

*Methyl bis-*p*-nitrophenoxyethanetetracarboxylate*, $C_{22}H_{20}O_{14}N_2$, crystallises in colourless leaflets or prisms, m. p. 203°, and on hydrolysis yields *p*-nitrophenol and a small amount of colourless needles, m. p. 180—181°, resembling succinic acid. The *ethyl* ester,

$$C_{26}H_{28}O_{14}N_2,$$

crystallises in yellowish-white needles, m. p. 107—109°.

Methyl p*-nitrobenzylethanetetracarboxylate*, $C_{17}H_{19}O_{10}N$, crystallises in slightly yellow needles, m. p. 119—120°. G. Y.

2:6- and 2:7-Naphthalenedicarboxylic Acids. FELIX KAUFLER and OSKAR THIEN (*Ber.*, 1907, 40, 3257—3262).—The hydrolysis of the nitriles of 2:6- and of 2:7-naphthalenedicarboxylic acids by potassium hydroxide in amyl-alcoholic solution at 120° and 126° (Kaufler, Abstr., 1906, ii, 424) proceeds with the greater velocity in the case of the latter. Of the nitriles of the three phthalic acids, the hydrolysis of the meta-isomeride is most rapid, and that of the para-compound least.

Methyl 2:6-naphthalenedicarboxylate, m. p. 191°, and *methyl 2:7-naphthalenedicarboxylate*, m. p. 135—136°, prepared from the corresponding acid chlorides and methyl alcohol, were hydrolysed at 37° by an equivalent quantity of methyl-alcoholic potassium hydroxide; the rates of hydrolysis are practically equal, the same result being observed in the hydrolysis of methyl terephthalate and methyl *iso*phthalate under the same conditions.

The m. p's. of the *nitrile-carboxylic acids*, *-amides*, and *-anilides* are above 300°, with the exception of 2 : 7-naphthalenedicarboxydianilide, which has m. p. 297—298°. C. S.

A Benzoylpolypeptide from Asparagine. TAKAOKI SASAKI (*Beitr. chem. Physiol. Path.*, 1907, 10, 120—122).—Both alanine and asparagine, when heated with benzoic anhydride, yield products which give the biuret reaction, owing to the formation of polypeptides under the condensing influence of the anhydride.

Asparagine, kieselguhr, and benzoic anhydride, when heated at 110°, yield a product from which, after extraction in a Soxhlet apparatus, solution in water, and salting out, a *substance*, $C_{19}H_{24}O_8N_6$, has been isolated. It forms a hard mass which can be readily pulverised, decomposes at 210°, is soluble in warm water, dilute alcohol or aqueous acetone and acids or alkalis, but insoluble in dry organic solvents. It can be separated from its solutions by the addition of ammonium sulphate or zinc sulphate, and is precipitated by mercuric nitrate, ferric ammonium alum, basic lead acetate, and tannic acid, and by phosphotungstic and phosphomolybdic acids in acidified solutions. The compound probably contains one benzoyl and three asparagine residues. J. J. S.

Lichens and their Characteristic Constituents. XI. OSWALD HESSE (*J. pr. Chem.*, 1907, [ii], 76, 1—57. Compare Abstr., 1906, i, 280).—The lichens treated of in the latter parts of this investigation have been extracted successively with ether and almost boiling acetone, or, in some cases, chloroform, without preliminary pulverisation.

Usnea articulata var. intestiniformis, from East Indian cinchona bark, contains *d*-usnic acid, about 1% of barbatic acid, and *articulatic acid*, $C_{18}H_{16}O_{10}$(?), which crystallises in colourless leaflets, sinters at 260°, becoming black, has a bitter flavour, gives a brownish-red coloration with alcoholic ferric chloride, and dissolves in alkalis, alkali carbonates, or concentrated sulphuric acid, forming yellow solutions gradually becoming reddish- or dark brown; it differs from protocetraric and ramalic acids in not giving a coloration when heated with alcohol and small amounts of sulphuric acid.

Ramalina armorica contains atranorin, 0·9% of armoricaic acid, and 1·4% of armoric acid.

Armoricaic acid crystallises from alcohol or glacial acetic acid in microscopic needles, decomp. 240—260°, has an intensely bitter flavour, reddens blue litmus, gives a brownish-red coloration with alcoholic ferric chloride, dissolves in alkalis, forming yellow solutions which gradually become red, and gives with hot concentrated sulphuric acid a reddish-brown coloration, becoming purple and finally dark red.

Armoric acid, $C_{18}H_{18}O_7,H_2O$, crystallises in long leaflets, loses H_2O at 100°, m. p. 226—228° (decomp.), gives with alcoholic ferric chloride a bluish-violet, or with hot concentrated sulphuric acid an intense green, coloration, and when boiled with aqueous baryta yields betorcinol and evernic acid.

Evernuric acid, m. p. 200° (191—192°: Abstr., 1903, i, 702), which, contrary to Zopf's statement, is not identical with physodic acid, has been obtained in varying amounts from eight specimens of *Evernia furfuracea var. ceratea*; the amorphous *triacetate*, $C_{24}H_{23}O_9Ac_3$, has m. p. 66—68°. This lichen contains also physodylic acid and a substance, probably Zopf's supposed furfuracic acid, which is decolorised by animal charcoal in ethereal solution, and yields a white, crystalline *acid*, m. p. 118°, resembling furevernic acid and hence termed *fureverninic acid*.

Physodylic acid, $C_{23}H_{26}O_8$, crystallises in white needles, m. p. 192°, is tasteless, has an acid reaction in alcoholic solution, gives a bluish-green coloration with ferric chloride, forms colourless alkaline solutions, which rapidly become yellow and finally reddish-brown, is decomposed when heated with hydrogen iodide, D 1·7, and yields a red, amorphous *potassium* salt. A brown, amorphous *modification* of the acid is obtained by evaporation of the aqueous solution of the potassium salt at 30°. When boiled with aqueous baryta, the acid forms barium carbonate and amorphous *physodol*, $C_{22}H_{26}O_6$, m. p. above 120°, which in alcoholic solution gives with ferric chloride a violet, or with calcium hypochlorite a dark red, coloration. Acetylation of the acid leads to the formation of *diacetylphysodic acid*, $C_{23}H_{22}O_7Ac_2$, white needles, m. p. 158°, and *triacetylphysodic acid*, $C_{23}H_{21}O_7Ac_3$, m. p. 74°. Physodic acid, $C_{23}H_{24}O_7$, is considered to be physodylic anhydride.

Parmelia physodes var. vulgaris has been reinvestigated and found to contain evernuric, physodylic, and capraric acids and traces of atranorin, but not physodic acid or physol (compare Abstr., 1898, i, 680; Zopf, Abstr., 1897, i, 436).

Menegazzia pertusa (*Parmelia pertusa*) contains atranorin and small amounts of a white crystalline *substance*, which is insoluble in potassium carbonate, and of amorphous farinacic acid; capraric and physodic acids (Zopf, Abstr., 1898, i, 489) were not obtained. The crystalline acid, m. p. 198°, obtained from this lichen by Zopf (*loc. cit.*), could not be physodic acid, as it gave a violet coloration with ferric chloride, but was probably farinacic acid.

Zopf's destrictic acid (Abstr., 1903, i, 763) is found to be an alkaline derivative of the pigment of *Cladina destricta*; a small amount of blue crystals, obtained from the chloroform solution, consisted of an unstable compound of the pigment with a substance which might be squamatic acid.

Cladonia rangiferina var. silvatica (*Cladina A silvatica*), gathered at a height of about 2400 m. on the Vorarlberg, contains *d*-usnic and *silvatic* acids, but not *l*-usnic, protocetraric, or fumarprotocetraric acids (compare Abstr., 1898, i, 533; 1899, i, 381; Widman, Abstr., 1900, i, 235; Zopf, Abstr., 1906, i, 672).

Silvatic acid, $CO_2Me\cdot C_{18}H_{34}O_3\cdot CO_2H$, crystallises in needles, m. p. 100—102°, and forms a crystalline *potassium* salt. *Norsilvatic acid*, $C_{20}H_{36}O_7$, formed together with methyl iodide when silvatic acid is heated with hydrogen iodide, D 1·7, is obtained as a white, crystalline powder, m. p. 109°, forms amorphous *salts*, and on prolonged heating at 60—80° is converted partially into an *acid* crystallising in needles, m. p. 128°.

Cetraria islandica contains, in addition to protolichesteric, $[\alpha]_D^{20}$ + 22·7°, and proto-α-lichesteric acids, an *acid* containing smaller percentages of carbon and hydrogen. The same lichen, from above the tree limit in Osterdalen in Norway, contains proto-α-lichesteric, but not protolichesteric, acid. When boiled with aqueous baryta, protolichesteric acid yields barium carbonate and a *substance*, m. p. 280—285° (decomp.), which on solution in glacial acetic acid is converted into an *acid*, crystallising in needles, m. p. 100—101°.

Physcion is contained in *Tornabenia chrysophthalma*, from the neighbourhood of Heidelberg, and *T. flavicans var. crocea*, from Lindi, German East Africa.

T. flavicans var. acromela (*Physcia acromela*), from Amani, German East Africa, contains *acromelin* and *acromelidin*. *T. flavicans var. cinerascens*, from Amani, and *T. flavicans*, from East Usambara, which is identical with *Teloschistes flavicans* from Brittany, contain physcion and acromelin.

Acromelin, $C_{17}H_{16}O_9$, is a lactone; it crystallises in colourless needles, m. p. 242°, is converted slowly by potassium hydroxide into a gelatinous *potassium* salt of the corresponding acid, forms barium carbonate on prolonged boiling with aqueous baryta, is reduced by hydrogen iodide, D 1·7, to a brown flocculent *substance*, and on treatment with hot concentrated sulphuric acid forms a blackish-brown, amorphous *substance*, which dissolves to a greenish-blue solution. iso*Acromelin*,

$C_{17}H_{16}O_9$, formed on heating acromelin with acetic anhydride, crystallises in colourless leaflets, m. p. 188°, and, when boiled with aqueous baryta, yields *acromelol*, $C_{16}H_{18}O_8$, crystallising in colourless prisms, m. p. 134°.

Acromelidin, $C_{19}H_{20}O_9$, forms slightly yellow, granular crystals, m. p. 162°, and gives with alkalis a rose-red, or with hot concentrated sulphuric acid a greenish-blue, coloration.

Physcia leucomelas, from Amani, contains atranorin and an *acid*, which crystallises in leaflets, m. p. 175°, and gives a brownish-red coloration with alcoholic ferric chloride.

The occurrence of lecanoric acid in *Urceolaria scruposa var. vulgaris* is confirmed. Zopf's diploschistessic acid (Abstr., 1906, i, 672) is considered to be a mixture of 80% of lecanoric acid and 20% of an acid, which gives a blue coloration with calcium hydroxide and for which it is suggested Weigelt's term patellaric acid may be retained.

Hämatomma coccineum var. abortivum does not contain zeorin. Small amounts of lecanoric acid, obtained from *Hämatomma coccineum var.* (?) (Abstr., 1906, i, 281), may have been derived from an admixture of the sterile lichen which could not be avoided entirely.

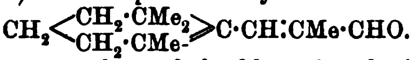
Biatora lucida contains atranorin in addition to the rhizocarpic acid found by Zopf.

Rhizocarpon geographicum (L.) DC. *f. geronticum*, from Rossegtal in the Engadine, contains parellic and rhizocarpic acids, but not rhizocarpinic acid (Abstr., 1899, i, 384). Ethyl norrhizocarpate, $C_{24}H_{16}O_8(CO_2Et)_2$, m. p. 171° (159°: *loc. cit.*). The rhizocarpinic acid, m. p. 170°, referred to by Zopf (Abstr., 1906, i, 672), had been shown to be non-existent before the description under the same name of the acid, m. p. 156° (Abstr., 1899, i, 384). G. Y.

Synthesis of an Aldehyde with the Odour of Violets. β-*cyclo*Citralidenepropenal. PHILLIPE BARBIER (*Compt. rend.*, 1907, **144**, 1442—1443).—By treating an aqueous alcoholic solution of citral and propaldehyde in molecular proportions with dilute soda, an odourless, oily liquid is obtained, which can be separated into two fractions: (1) b. p. 147—148°/13 mm., and (2) b. p. 158—160°/13 mm., having the same composition, $C_{13}H_{20}O$. From the method of formation, the resulting aldehyde should be *βει-trimethyl-$\Delta^{\beta\delta\theta}$-decatriene-a-al*,

$$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH{:}CMe\cdot CHO.$$

By dissolving the latter in 60% sulphuric acid, heating at 50—60° for a few minutes, and pouring on to ice, an oily liquid is formed, which also can be separated into two fractions, both of the same composition. The constitution of the cyclic aldehydes (β-cyclo-*citralidenepropenal*) can be represented by the formula



$$CH_2{<}\begin{matrix}CH_2\cdot CMe_2\\ CH_2\cdot CMe{=}\end{matrix}{>}C\cdot CH{:}CMe\cdot CHO.$$

They have an intense odour of freshly-gathered violets. The two fractions give two *semicarbazones*, one forming crystals, m. p. 174—175°, the other viscous. The aldehydes have no commercial value, owing to the rapidity with which they oxidise. E. H.

Condensation of *p*-Dimethylaminobenzaldehyde with Dibenzyl Ketone and Phenylacetone. Ernst Mayerhofer (*Monatsh.*, 1907, **28**, 589—604. Compare Schimetschek, Abstr., 1906, i, 368).—Both dibenzyl ketone and phenylacetone condense with *p*-dimethylaminobenzaldehyde under the influence of hydrogen chloride in benzene solution with the formation, in each case, of two unsaturated ketones.

p-*Dimethylaminobenzylidenedibenzyl ketone*, $NMe_2\cdot C_6H_4\cdot CH\colon CPh\cdot CO\cdot CH_2Ph$, crystallises in brilliant, canary-yellow, prismatic needles, m. p. 118—119°; the *hydrochloride* forms colourless crystals; the *dibromide* could not be obtained in a crystalline form. The *oxime*, $C_{24}H_{24}ON_2$, prepared by the action of hydroxylamine hydrochloride on the ketone, crystallises in almost pure, white needles, m. p. 184—185°; it does not reduce Fehling's solution.

p-*Dimethylaminohydroxylaminobenzyldibenzyl ketone*, $NMe_2\cdot C_6H_4\cdot CH(NH\cdot OH)\cdot CHPh\cdot CO\cdot CH_2Ph$, is obtained by treating the ketone with hydroxylamine hydrochloride in the presence of sodium acetate; it crystallises in almost white needles, m. p. 156° (decomp.), and reduces Fehling's solution.

Di-p-*dimethylaminobenzylidenedibenzyl ketone*, $(NMe_2\cdot C_6H_4\cdot CH\colon CPh)_2CO$, forms greenish-yellow crystals, m. p. 211°; the *hydrochloride* forms colourless crystals. This ketone does not give an oxime.

p-*Dimethylaminobenzylidenephenylacetone* forms yellow crystals, m. p. 70—71°; it could not be determined whether it has the formula $NMe_2\cdot C_6H_4\cdot CH\colon CPh\cdot COMe$ or $NMe_2\cdot C_6H_4\cdot CH\colon CH\cdot CO\cdot CH_2Ph$; the *hydrochloride* is colourless. The ketone is decomposed on treatment with bromine in chloroform solution, probably into acetyl bromide and p-*dimethylaminobromostilbene*, $NMe_2\cdot C_6H_4\cdot CH\colon CPhBr$, obtained as light yellow crystals, m. p. 98—92°. The *oxime*, $C_{18}H_{20}ON_2$, crystallises in brilliant, white needles, m. p. 181—182°; it does not reduce Fehling's solution.

Di-p-*dimethylaminobenzylidenephenylacetone*, $NMe_2\cdot C_6H_4\cdot CH\colon CPh\cdot CO\cdot CH\colon CH\cdot C_6H_4\cdot NMe_2$, forms yellow crystals, m. p. 225·5°; the *hydrochloride* is colourless. An oxime could not be prepared. W. H. G.

***cyclo*Nonanone and *cyclo*Nonane.** Nicolai D. Zelinsky (*Ber.*, 1907, **40**, 3277—3279).—Dry distillation of sebacic acid yields in small quantities cyclo*nonanone*, $C_9H_{16}O$, an oil, b. p. 95—97°/17—18 mm., $D_4^{22\cdot5}$ 0·8665, $n_D^{22\cdot5}$ 1·4412, and volatile in steam; the *semicarbazone*, $C_{10}H_{10}ON_3$, has m. p. 105°. On reduction of the ketone by sodium, conversion into iodide, and reduction of the iodide by zinc, cyclo*nonane*, C_9H_{18}, is obtained as an oil, b. p. 170—172°, D_4^{16} 0·7733, n_D^{16} 1·4328. The molecular refraction of these two compounds is higher than the calculated value, owing to the ring formation. W. R.

Terpene and Benzoic Acid. Pietro Cesaris (*Boll. chim. farm.*, 1907, **46**, 495—496).—On dissolving terpene and benzoic acid in molecular proportions in an excess of boiling water, the solution deposits a readily volatile *substance* in broad, rectangular, shining plates, m. p. 97°; it has an aromatic odour and a sweetish taste, and dissolves in alcohol (6 : 100), glycerol or chloroform (0·05 : 5), and, to a slight extent, in ether (0·01 : 15). It gives no characteristic reaction with sulphuric, hydrochloric, or nitric acid or ferric chloride.

T. H. P.

Constituents of Ethereal Oils. The Sesquiterpenes Present in East Indian Sandal-Wood Oil. FRIEDRICH W. SEMMLER (*Ber.*, 1907, **40**, 3321—3224. Compare this vol., i, 714; also von Soden and Müller, Abstr., 1899, i, 924; Guerbet, Abstr., 1900, i, 242, 401).—α-Santalene has b. p. 118—120°/9 mm., D^{20} 0·8984, n_D 1·491, α_D $-15°$ (100 mm.). β-Santalene has b. p. 125—127°/9 mm., D^{20} 0·892, n_D 1·4932, and α_D $-35°$. These properties correspond closely with those of the α- and β-santalols.

When oxidised with ozone in benzene solution, α-santalene yields tri*cyclo*eksantaldehyde (this vol., i, 431), and the nitrile of tri*cyclo*-eksantalic acid (*loc. cit.*), when reduced with sodium and alcohol, yields *tri*cyclo*eksantalamine*, $C_{11}H_{17}\cdot NH_2$. This has b. p. 113—116°/9 mm., D^{20} 0·94, n_D 1·4895, and α_D $+4°30'$ (100 mm.). The *picrate*, $C_{11}H_{17}NH_2,C_6H_3O_7N_3$, has m. p. 183—184°.

β-Santalene, when oxidised in a similar manner, yields an aldehyde from which di*cyclo*eksantalic acid, m. p. 64° (this vol., i, 432), has been obtained.

J. J. S.

Ethereal Oils. HEINRICH HAENSEL (*Chem. Zentr.*, 1907, i, 1332; from *Geschäftsber.*, March, 1907. Compare Abstr., 1906, i, 524).—Traces of an aldehyde have been found in a rhododendron oil, which has D^{18} 0·8620, α_D^{18} $-4·33°$; the saponification number of the oil from which the aldehyde has been removed is 20·5, and that of the acetyl derivative, 36·2. The fraction of b. p. 150—160°/742 mm. yields a small quantity of a nitrosochloride of m. p. 102—103°, which does not react with piperidine or benzylamine. Cineol could not be detected in the oil.

A sample of camomile oil, which has D^{15} 0·9368, acid number, 24·2, and saponification number, 55·7 (acetyl derivative, 117·7), contains nonolic acid, but neither aldehydes nor phenols. The oil boils at 100—250°/10—12 mm. and forms a considerable quantity of resin. None of the fractions appear to contain alcoholic substances.

Grindelia oil, prepared from *Grindelia robusta*, is brown and has a strong odour; it has D^{15} 0·9582, α_D $-8·08°$ in alcoholic solution, saponification number, 75·1 (acetyl derivative, 162·1), and contains borneol and about 8% of a brown oil which has the character of a phenol.

German curled mint oil contains *l*-carvone, dipentene, and cineol.

Opoponax oil is greenish-yellow and has a strong, persistent odour; it has D^{15} 0·9154, α_D $-13·94°$, acid number, 2·7, saponification number, 17·3 (acetyl derivative 75·6), and b. p. 80—195°/16 mm. Attempts to isolate alcoholic substances failed.

Heptoic acid has been detected in parsnip oil and butyric acid is probably present.

E. W. W.

Ethereal Oils. SCHIMMEL & Co. (*Chem. Zentr.*, 1907, i, 1413—1414; from *Geschäftsber.*, April, 1907. Compare Abstr., 1906, i, 524).—Ayapana oil or essence d'Ayapana, prepared from *Eupatorium triplinerve*, is pale green and has a peculiar odour; D^{15} 0·9808, $a_D+3°10'$, ester number, 8·0 (acetyl derivative, 23·4), and consists mainly of a homogeneous substance, which has b. p. 237—238°/750 mm. and D^{15} 0·9891. The latter compound is attacked by potassium permanganate with difficulty, yielding an acid of m. p. 93°.

Oil of cassia flowers, prepared from a French extract, has D^{15} 1·0575, a_D $-0°30'$, n_D^{22} 1·51500, acid number, 25·4, and ester number, 22·9.

The constants quoted for the sesquiterpene alcohol from copaiva oil (Abstr., 1906, i, 524) correspond with those of the hydrocarbon obtained from the alcohol by the action of formic acid.

A fraction of elemi oil, which had D^{15} 1·025, a_D $+2°15'$, and saponification number, 2·8 (acetyl derivative, 81·4), yielded a fraction which probably consisted of alcohols; the acetyl derivative had the odour of curled mint oil, but did not appear to contain the acetate of dihydrocumin alcohol. By the action of concentrated formic acid on the higher fractions of b. p. 277—278°, a hydrocarbon is obtained, which on oxidation with potassium permanganate yields an *acid*, $C_{12}H_{16}O_6$, of m. p. 167·5—169°. The acid crystallised from dilute alcohol in needles and from benzene in prisms; *silver* salt, m. p. 192—193°. Rectified fir-cone oil, prepared from cones of *Picea excelsa*, is greenish-yellow and has a stale and somewhat musty odour; it has D^{15} 0·8743, a_D $-19°15'$, acid number, 1·8, ester number, 3·9, corresponding with 1·4% bornyl acetate.

The components of iris oil, which are more volatile than irone, form a golden-yellow oil which has an unpleasant basic odour somewhat resembling that of scatole. The oil contains furfuraldehyde, decaldehyde, nonaldehyde, naphthalene, a terpene of D^{15} 0·8611, a_D $+10°40'$, a *ketone*, $C_{10}H_{18}O$, which has an odour resembling that of mint (*semicarbazone*, m. p. 217—218°), and traces of a base, a phenol, and of an alcohol which reacts with phthalic acid. The oleic acid aldehyde which Tiemann and Krüger found in iris oil, prepared by extraction, is not contained in the distilled oil. The aldehyde, prepared by distilling calcium oleate and formate, has a rather faint odour and, on cooling, forms a wax-like mass; it has b. p. 168—169°/3—4 mm., D^{15} 0·8513, n_D^{20} 1·45571, and yields a semicarbazone of m. p. 87—89°.

The composition of kuromoji oil is somewhat variable, probably because different samples are prepared from different portions of the plant; it has D^{15} 0·8942, $a_D-7°35'$, and ester number, 27·3, and is a slightly yellow oil with an odour similar to that of coriander; it contains terpenes, cineol, linalool, and geraniol, the last being present mainly in the form of the acetate.

Experiments on the distillation of lavender oil have shown that when the best yield is obtained by using fresh flowers and distilling as rapidly as possible in steam, the oil is richest in esters, and also differs from the ordinary oil in other properties.

The oil from *Mentha rotundifolia* is dark orange yellow, and has a faint musty odour somewhat like that of curled mint; it has

D^{15} 0·9777, $\alpha_D - 37°30'$, acid number, 1·5, and ester number, 71·2 (acetyl derivative, 209).

Myrtle oil, on distillation, yields pinene and a hydrocarbon which behaves like camphene.

Two samples of origanum oil, from Cyprus, had D^{15} 0·9624, 0·9655, $\alpha_D + 0°20'$, 0°, and contained 77% and 70% of phenol respectively; a Syrian oil had D^{15} 0·936—0·960, α_D 0 to $+1°35'$, and contained 65—72% of phenol, and corresponded with the ordinary Spanish hop oil.

Thyme lemon oil is orange-yellow and has the odour of lemon oil with a slight admixture of thyme oil; it has D^{15} 0·9085, $\alpha_D + 9°45'$.

Vetiver oil, from E. African roots, is identical with that obtained from other sources, and forms a brown oil which has a strong odour; it has D^{15} 1·0166, $\alpha_D + 36°35'$, acid number, 40, and ester number, 22·8.

The rotatory power of juniper oil, distilled from berries and needles, differs from that of the ordinary oil; it has D^{15} 0·8675, $\alpha_D + 8°46'$, and ester number, 11·4.

The following new oils are described. A yellowish-green ethereal oil from *Xanthoxylum aubertia* (*Evodia aubertia of Cordemoy*; *Rutaceæ*), from Réunion, has a distinct odour of parsley, but does not contain phellandrene; it has D^{15} 0·9052, $\alpha_D - 62°10'$, acid number, 1·3, and ester number, 7·3 (acetyl derivative, 51). The properties of a second sample, which had a similar odour, very closely resembled those of the oil from *Evodia simplex* (*loc. cit.*); it had D^{15} 0·9708, $\alpha_D - 19°20'$, acid number, 1·1, and ester number, 8·7 (acetyl derivative, 33).

A sample of pilea oil had a green tinge and was considerably more dextrorotatory than that previously described (*loc. cit.*), but resembled it in other properties; it had D^{15} 0·8520, $\alpha_D + 58°20'$, n_D^{20} 1·46902, acid number, 0, and ester number, 7·7 (acetyl derivative, 34·4). A pale yellow ethereal oil has been obtained by distilling the buds of black currants (*Ribes nigrum*); it had D^{15} 0·8741, $\alpha_D + 2°30'$, n_D^{20} 1·48585, acid number, 0, and ester number, 5·6. The odour of the oil suggested the presence of cymene. E. W. W.

Lupeol. ÉMILE JUNGFLEISCH and HENRI LEROUX (*Compt. rend.*, 1907, **144**, 1435—1437. Compare Abstr., 1906, i, 525).—From the gutta-percha of *Palaquium Treubi*, the authors have isolated a substance crystallising in monoclinic needles (Wyrouboff), having α_D +50·0° in a 1% solution in chloroform, apparently identical with the lupeol cinnamate found by van Romburgh in other guttas (Abstr., 1904, i, 905). The lupeol obtained from it, when heated gradually on the Maquenne block, melts at 212°, but when thrown suddenly on the heated block it melts at 190—192°, quickly resolidifies, and on continued heating re-melts at 212°. This behaviour, which explains the difference in melting points observed by different authors, is due to the lupeol losing water and forming a hydrocarbon. The lupeol has m. p. 190—192°, whilst the hydrocarbon, *lupeylene*, which crystallises in fine needles, has m. p. 212°, and α_D 24·57°. The dehydration of lupeol occurs slowly at 130°, but very rapidly at 150—160°, and this is probably the explanation of the fact that Likiernik (Abstr., 1891, 551, 1446) and later Cohen (this vol., i, 211) obtained an acetate,

m. p. 223°, and a monobromo-derivative, m. p. 185°, whilst Sack and Tollens (Abstr., 1904, i, 1011), who were probably dealing with lupeylene, failed to obtained an acetate and obtained a dibromo-derivative, m. p. 154°. By the action of bromine on lupeol, the authors obtained Likiernik's monobromo-derivative, with evolution of hydrogen bromide, whilst from lupeylene they obtained Sack and Tollens' dibromo-derivative, m. p. 160°, without evolution of hydrogen bromide. Instead of the formula $C_{26}H_{42}O$, suggested by Likiernik, or $C_{31}H_{50}O$, proposed by Cohen, for lupeol, the authors suggest the formula $C_{30}H_{50}O$, identical with that of the amyrins and paltreubin. This is supported by the molecular weight of lupeol, 406—412, and of its cinnamate, 540—543.

The lupeol isolated from bresk or djetulung is also decomposed by heat into water and hydrocarbon. E. H.

Isomerism of the Hydrogen Cyanide Glucosides, Sambunigrin and Prulaurasin. Émile Bourquelot and Henri Hérissey (*J. Pharm. Chim.*, 1907, [vi], **26**, 5—12).—The authors discuss the isomerism of (1) amygdalin and *iso*amygdalin and (2) Fischer's mandelonitrile glucoside, prulaurasin, and sambunigrin.

When treated with concentrated hydrochloric acid, amygdalin yields ammonia, dextrose, and *l*-mandelic acid, whilst with *iso*amygdalin, *r*-mandelic acid is obtained.

Dunstan and Henry (*Brit. Ass. Rep.*, 1906) stated that the differences between the three mandelonitrile glucosides, assuming that they are different, lie probably in the nature of the residual sugars. It had, however, previously been shown that the three glucosides are chemically distinct individuals and that the sugar yielded by sambunigrin (Bourquelot and Danjou, Abstr., 1905, i, 912) and by prulaurasin (Hérissey, Abstr., 1906, i, 31) is identical with dextrose. The authors show that, when hydrolysed by hydrochloric acid, Fischer's mandelonitrile glucoside yields *l*-mandelic acid, whilst sambunigrin gives *d*-mandelic acid. They find also that, when sambunigrin is racemised by the action of a small quantity of barium hydroxide solution, it is converted into prulaurasin, which, when hydrolysed with hydrochloric acid, yields *r*-mandelic acid.

T. H. P.

Chlorophyll. III. Action of Acids and Alkalis on Chlorophyll. Richard Willstätter and Ferdinand Hocheder (*Annalen*, 1907, **354**, 205—258. Compare this vol., i, 69, 71).—Chlorophyll is a complex magnesium compound. The authors have been able, by treatment of alcoholic solutions of chlorophyll with the calculated amount of oxalic acid, to remove the magnesium quantitatively and to obtain for the first time an ashless compound closely related to chlorophyll. This derivative is an *ester*, termed *phaeophytin*, and is hydrolysed readily by alkalis, yielding an unsaturated alcohol, *phytol*, $C_{20}H_{40}O$, which is formed also by the action of alkalis on chlorophyll. For the hypothetical saturated hydrocarbon, corresponding with this alcohol, the authors propose the name *phytane*, and for the coloured, nitrogenous nucleus of chlorophyll, the name *phytochromin*; the phytochlorins and phytorhodins are phytochromin derivatives.

Phaeophytin is obtained in nearly quantitative yields as an almost black, wax-like substance, or occasionally in needles, m. p. 133—138° (decomp.), evolves a vapour with an odour of tobacco when strongly heated, can be purified by solution in boiling alcohol, from which it separates on cooling, is dark olive-brown with a slight red fluorescence in solution, and resembles chlorophyll in forming green to blue complex *salts* when treated with zinc, copper, or ferric acetate in glacial acetic acid solution; the zinc and ferric salts are fluorescent. Phaeophytin is an indifferent substance, and does not react with alkalis or dilute mineral acids in ethereal solution, but is decomposed in ethereal solution by 30% sulphuric acid, or when solid by concentrated acids, gives a blue coloration with concentrated nitric acid in ethereal or glacial acetic acid solution, forms an intense green solution with bromine in chloroform, and has a characteristic absorption spectrum. The composition of phaeophytin varies slightly with the source of the chlorophyll and the time of year at which the leaves are gathered; it yields about 30% of its weight of phytol, and has an equivalent weight of 219—230, calculated from its percentage of nitrogen. From these results, the molecular formula is calculated to be approximately $C_{50}H_{70}O_5N_4$, $C_{54}H_{72}O_5N_4$, or $C_{56}H_{76}O_6N_4$.

The identity of the chlorophylls from different plants is questioned, and it is concluded that there is not one chlorophyll, but a group of similar substances differing in the phytochromin nucleus.

The hydrolysis of phaeophytin leads to the formation of phytol together with phytochlorins and phytorhodins, which have been isolated in the manner described previously. Phaeophytin, obtained from the stinging nettle, yields on hydrolysis with hot concentrated hydrochloric acid a phytorhodin (7), or with cold concentrated hydrochloric acid chiefly a phytochlorin (11) together with a phytochlorin (17), or with hot alcoholic potassium hydroxide, phytochlorins (1, 3, and 11) together with small amounts of a phytorhodin (7) and more feebly basic substances (13 and 20). The numbers given in brackets are the percentage strengths of the hydrochloric acid by which the bases are extracted from their solutions in ether.

Phaeophytin, obtained from grass, yields on hydrolysis chiefly *phytochlorin e* and *phytorhodin g*, whilst that from green algæ yields *phytochlorin f* and *phytorhodin h*.

Phytochlorin e, $C_{30}H_{32}O_4N_4$, is extracted from its ethereal solution by 3% hydrochloric acid when freshly prepared, but by 12% acid after being dried; it forms black, microcrystalline aggregates, does not melt at 300°, is soluble in acids or alkalis, forming coloured solutions, and yields an intense green *copper* compound with copper acetate in glacial acetic acid solution.

Phytochlorin f, $C_{31}H_{32}O_4N_4$, is extracted from ether by 12% hydrochloric acid; it crystallises in black plates, is green by transmitted light, sinters and decomposes at 265—270°, and when dried is dissolved only by 17—20% acid, but regains its colour and basicity on solution.

Phytorhodin g, $C_{30}H_{32}O_6N_4$, crystallises in stout, dark red prisms, commences to sinter at 250°, does not melt, is soluble in ammonia or dilute acids, forming coloured solutions, and is extracted from its ethereal solution by 9%, but is dissolved when dry only by 17—20% hydrochloric acid.

Phytorhodin h is extracted from its ethereal solution by 4·5% hydrochloric acid, and crystallises in bluish-black, microscopic rosettes.

Phytol, $C_{20}H_{40}O$ ($C_{19}H_{38}O$?), is a colourless oil, b. p. 145°/0·03 mm., commences to decompose at 150—160°, D_4^0 0·864, D_4^{20} 0·852, and has a slight characteristic odour; the crude substance has $[\alpha]_D^{20}$ +0·79°, but after distillation is optically inactive. It is not reduced by sodium and alcohol, reduces potassium permanganate, forms an oily *additive* compound, together with traces of a crystalline *additive* compound, with 1 mol. of bromine in chloroform solution at 0°, yields small amounts of hydrogen bromide with an excess of bromine, and, when heated with phthalic anhydride at 170—180°, forms phthalic acid, and an *oil*, which is only sparingly soluble in methyl alcohol, is formed also by heating phytol with glacial acetic acid at 200°, and contains various high molecular, oxygenated compounds.

Phytol esterifies, by Menschutkin's method (Abstr., 1879, 36, 215), 65·6% of acetic acid in 144 hours at 98°, but only 36·2% in one hour at 155°, the yield diminishing on longer heating at the higher temperature. Under the same conditions, cetyl alcohol esterifies 47·8% of acetic acid in one and a quarter hours, and 75·7% in 145 hours at 155°. These results are compared with those obtained by Menschutkin for octyl and allyl alcohols, and are considered to show that phytol is a primary alcohol of the ethylene series.

The *sodium* derivative of phytol, $C_{20}H_{39}ONa$, differs from those of cetyl alcohol and cholesterol in that it is soluble in ether; it reacts with *p*-nitrobenzoyl chloride in ethereal solution forming *p*-nitrobenzoic anhydride. The *phenylurethane*, $C_{20}H_{39}O\cdot CO\cdot NHPh$, crystallises in colourless prisms, m. p. 25·8—28·8°. The *a-naphthylurethane*, $C_{20}H_{39}O\cdot CO\cdot NH\cdot C_{10}H_7$, formed together with small amounts of di-*a*-naphthylcarbamide by the action of phytol on *a*-naphthylcarbimide, crystallises in colourless needles, m. p. 23·5—29·5°. On oxidation with chromic acid, phytol yields an indifferent, viscid *oil*, $C_{20}H_{38}O_2$, and an oily *lactone-acid*, $C_{20}H_{34}O_3$, which forms a sparingly soluble, crystalline *barium* salt.

Phytene, $C_{20}H_{40}$, formed by reduction of phytol with hydrogen iodide in glacial acetic acid solution at the ordinary temperature, is obtained as a colourless, odourless, mobile *oil*, b. p. 106·5—108°/0·04—0·05 mm. or 167—168°/7·5 mm., D_4^0 0·817, reduces potassium permanganate slowly in glacial acetic acid solution, and forms an *additive* compound with 1 mol. of bromine.

The residues obtained on distillation of crude phytol, obtained from grass, closely resemble phytol, but that derived from phytol, prepared from nettles, yields a viscid *oil*, $C_{40}H_{78}O$ or $C_{40}H_{74}O$, which is sparingly soluble in methyl alcohol and is probably an ether of phytol or of a more unsaturated alcohol. Distillation of phytol under 1 mm. pressure leads to the formation of the *aldehyde*, $C_{20}H_{38}O$, which is obtained as an oil, and forms an oily *oxime*, whilst on distillation under higher pressures, the alcohol forms *phytadiene*, $C_{20}H_{38}$, b. p. 185—188°/22 mm.

G. Y.

The Chemistry of Chlorophyll, Phylloxanthin, Phyllocyanin, and the Chloropyllans. M. Tsvett (*Biochem. Zeitsch.*, 1907, 5, 6—32. Compare Abstr., 1900, i, 50, 67; 1901, i, 94, 222; 1906, i, 973; Marchlewski, this vol., i, 435).—By means of the adsorption analytical method already described (this vol., ii, 144), it can be shown that chlorophyll (that is, the total leaf pigment) consists of at least seven distinct colouring matters. Five of these, including carotin, are yellow, are not fluorescent, and do not show absorption bands in the red half of the spectrum. The two remaining pigments are the α- and β-chlorophyllins. The α-compound is present in larger quantity, and in concentrated ethereal solution has a pure indigo-blue colour, whereas β-chlorophyllin has a chlorophyll-green colour. Both compounds have six characteristic absorption bands between lines *B* and *G*. Each of the chlorophyllins is transformed into a characteristic derivative, α- and β-chlorophyllan, under the influence of dilute mineral acids. Hoppe-Seyler's chlorophyllan is a mixture of the two. Each has a characteristic absorption spectrum; they are not acidic, but their ethereal solutions when treated with potassium hydroxide solution undergo characteristic changes in colour. The chlorophyllins and chlorophyllans dissolve in concentrated mineral acids, but are, at the same time, decomposed. Schunck's phyllocyanin is the product formed by the action of hydrochloric acid on α-chlorophyllan, whereas phylloxanthin is derived from, if not identical with, β-chlorophyllan.

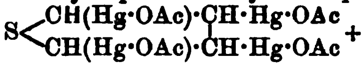
It has not been found possible to transform phylloxanthin into phyllocyanin. J. J. S.

Aniline-black. W. Nover (*Ber.*, 1907, 40, 3389).—A claim for priority as regards the investigation of emeraldine (compare this vol., i, 262, and Willstätter and Moore, *ibid.*, i, 641). J. J. S.

Action of a Solution of Iodine in Potassium Iodide on Some Basic Dyes. Louis Pelet and E. Gillièron (*Chem. Zentr.*, 1907, i, 1259; from *Schweiz. Woch. Chem. Pharm.*, 1907, 45, 88—90).—When a solution of iodine in potassium iodide is added to solutions of the hydrochlorides of safranine, magenta, chrysoidine, methylene-blue, phosphine, or muscarine, heavy, dark coloured precipitates of a di-iodohydriodide, M,HI,I_2, are formed; crystal-violet and auramine yield tri-iodohydriodides, M,HI,I_3. The dyes may be estimated volumetrically by means of this reaction. The precipitates may be dried at 50° without decomposition, and form black substances, some of which have a metallic lustre. All the iodohydriodides are very sparingly soluble in cold water, sparingly so in hot water or carbon disulphide, somewhat more readily soluble in acetone, alcohol, chloroform, nitrobenzene, or aniline, practically insoluble in benzene, toluene, or xylene, and rather readily soluble in cold mineral acids or alkalis; the solutions have the colours of the original dyes, but do not contain free iodine.

When tolusafranine and chrysoidine are treated with an excess of a solution of iodine in potassium iodide, tri-iodohydriodides are formed, and, under similar conditions, methylene-blue yields a tetraiodohydriodide.

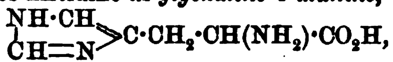
By the action of a concentrated solution of sodium hydrogen carbonate on the di-iodohydriodide of tolusafranine for five days, 1 atom of iodine is removed and the tetraiodohydriodide of methylene-blue also loses 1 atom of iodine when extracted sixty times with chloroform; the latter compound is not attacked, however, by sodium hydrogen carbonate. E. W. W.

Thiophen. VINCENZO PAOLINI (*Gazzetta*, 1907, 37, i, 58—62).—The compound formed by the action of saturated aqueous mercuric acetate solution on thiophen is found to have the formula $C_4H_4S(Hg{\cdot}OAc)_4$ (compare Dimroth, Abstr., 1899, i, 428), the reaction being probably represented by the equation: $C_4H_4S + 4Hg(OAc)_2 + 2H_2O =$  $S<\begin{matrix}CH(Hg{\cdot}OAc){\cdot}CH{\cdot}Hg{\cdot}OAc\\ CH(Hg{\cdot}OAc){\cdot}CH{\cdot}Hg{\cdot}OAc\end{matrix}$ $+ 4C_2H_4O_2 + O_2$; the oxygen formed is not liberated, but is used up in oxidising about one-half of the thiophen.

When treated with sodium chloride, the compound $C_4H_4S(Hg{\cdot}OAc)_4$ yields the corresponding *mercuric chloride* derivative, $C_4H_4S(HgCl)_4$, which is a white, microcrystalline powder insoluble in all the neutral solvents and in acetic acid, and gives the indophenine reaction with isatin and sulphuric acid; it is gradually decomposed by light, is reduced to thiophen by zinc and sodium hydroxide, and does not melt at 270°. The corresponding *bromo*-compound, $C_4H_4S(HgBr)_4$, is a white, microcrystalline powder, and the *iodo*-compound, $C_4H_4S(HgI)_4$, a yellow powder. When boiled with aqueous alkali hydroxide solution, the mercuric chloride derivative is converted into the corresponding *hydroxy*-compound, $C_4H_4S(Hg{\cdot}OH)_4$, which is a brown, basic substance, exploding with formation of a mercury mirror when warmed, and yielding the mercuric acetate derivative when treated with acetic acid. T. H. P.

Picrolonates of Certain Nuclein Bases. PHŒBUS A. LEVENE (*Biochem. Zeitsch.*, 1907, 4, 320—321. Compare Steudel, Abstr., 1903, i, 431; Otori, *ibid.*, 1905, i, 126).—*Adenine picrolonate*, $C_5H_5N_5,C_{10}H_8O_5N_4$, crystallises from water and melts at 265°. *Guanine picrolonate*, $C_5H_5ON_5,2C_{10}H_8O_5N_4$, and *cytosine picrolonate*, $C_4H_6N_3,C_{10}H_8O_5N_4$, have also been prepared and analysed. J. J. S.

Degradation and Constitution of Histidine. FRANZ KNOOP (*Beitr. chem. Physiol. Path.*, 1907, 10, 111—119. Compare Knoop and Windaus, Abstr., 1905, i, 834; Fränkel, *ibid.*, 1906, i, 547).—The constitution of histidine as *glyoxaline-4-alanine*,



has been established by the oxidation of oxydeaminohistidine to free glyoxaline. The first product obtained by boiling the oxydeaminohistidine with nitric acid (4 : 1) for six hours is *glyoxaline-4-glyoxylic acid*, $C_5H_4O_3N_2$. It has no definite m. p., but begins to turn brown at 220°, and is completely charred at 290°. The *oxime*, $C_5H_5O_3N_3$, crystallises in colourless needles, m. p. 229°. Histidine itself yields the same product when oxidised, but is not so readily attacked.

Glyoxaline-4-carboxylic acid, $C_4H_4O_2N_2$, is obtained when a dilute acetic acid solution of the glyoxylic acid is oxidised with hydrogen peroxide at the ordinary temperature. It crystallises in needles and decomposes at 286°, yielding glyoxaline. The same acid has been synthesised from tartaric acid.

The oxidation of oxydeaminohistidine in sulphuric acid solution with barium permanganate yields *glyoxaline-4-acetic acid*,

$$C_5H_6O_2N_2,H_2O,$$

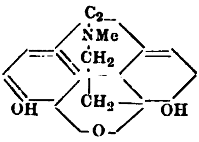
which crystallises from water in flat needles, m. p. 220° (decomp.).

J. J. S.

Morphine. XII. The Point of Attachment of the Side-Ring Containing Nitrogen in Codeine and the Constitution of Morphine Alkaloids. LUDWIG KNORR and HEINRICH HÖRLEIN (*Ber.*, 1907, **40**, 3341—3355. Compare Pschorr and Einbeck, this vol., i, 547).—Schryver and Lees' *iso*codeine (Trans., 1901, **79**, 576; this vol., i, 547) is a mixture of two bases, the one with m. p. 145° and the other 170° (compare Lees and Tutin, Proc., 1906, 253; Lees, Trans., 1907, **91**, 1408). The base of high melting point is shown to be identical with ψ-codeine (Merck, Abstr., 1891, 1121). The ketone obtained by oxidising ψ-codeine and Schryver and Lees' *iso*codeine is termed ψ-codeinone, as it undoubtedly corresponds with ψ-codeine.

ψ-Codeinone methiodide, when heated with alcohol, undergoes decomposition in a manner similar to codeinone methiodide (Knorr, Abstr., 1904, i, 916), yielding a dihydroxymethoxyphenanthrene, which on methylation gives 1:5:6-trimethoxyphenanthrene (Pschorr, Abstr., 1900, i, 234). ψ-Codeinone thus contains the carbonyl oxygen in position 1, and by the conversion of codeine into ψ-codeine a wandering of the alcoholic hydroxyl group from 3 to 1 occurs. The point of union of the side-ring remains unaffected during this change, since both codeine and ψ-codeine yield the same deoxycodeine. It follows that in ψ-codeine, morphine, codeine, and thebaine, the carbon chain of the side-ring cannot be attached to position 1. This position in the morphine alkaloids is not substituted, and in the formation of *apo*morphine from morphine the carbon chain of the side-ring is freed from its original attachment, and only as a secondary process becomes united to carbon atom 1.

The formation of *apo*morphine is thus a more complex reaction than as stated by Pschorr. Similarly, the side-ring cannot be attached to position 3, and, since it can be shown by Claisen's methods that both codeinone and ψ-codeinone contain the group $\cdot CO\cdot CH_2\cdot$, position 7 must be a methylene group. The conclusion is drawn that the bridge $\cdot CH_2\cdot CH_2\cdot NMe\cdot$ is attached, on the one side, to position 4 in the reduced benzene ring and, on the other, to position 9 or 10, probably 10, and the annexed formula is suggested for morphine. The constitution of morphine, codeine, and thebaine is thus quite distinct from that of the other opium bases, papaverine, narcotine, and laudanosine.



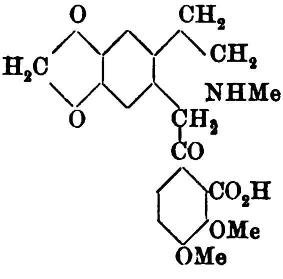
ψ-Codeinone condenses with benzaldehyde in dry ethereal solution in the presence of sodium ethoxide, yielding *benzylidene-ψ-codeinone* in the form of an oil. Its *methiodide*, $C_{25}H_{23}O_3N,MeI$, crystallises from methyl alcohol in rectangular needles and plates, and decomposes at about 250°. ψ-Codeinone also yields an iso*nitroso*-derivative, $C_{18}H_{18}O_4N_2$, in the form of a yellow powder which begins to blacken at 200°.

ψ-Codeinone, in contradistinction from codeine and ψ-codeine, reacts with solutions of diazonium salts, yielding dyes which are to be regarded as hydrazones of ψ-codeine-1 : 2-dione. With diazobenzene chloride, a red product is obtained. Codeinone also condenses with diazo-salts; with diazobenzene chloride in acetic acid solution, the red crystalline compound, $C_{24}H_{23}O_3N_3,CH_3\cdot CO_2H$, is obtained, m. p. 210—220° (decomp.). J. J. S.

Morphine. XIII. Action of Oxalic Acid on Codeine. LUDWIG KNORR and PAUL ROTH (*Ber.*, 1907, 40, 3355—3358. Compare Beckett and Wright, this Journ., 1875, 28, 696).—When perfectly dry codeine is heated with anhydrous oxalic acid at 150°; it yields a mixture of ψ-codeine (Merck, Abstr., 1891, 1121; Knorr and Hörlein, this vol., i, 151) and a new compound, ψ-apo*codeine*, $C_{18}H_{19}O_2N$. The two compounds may be separated by means of alcohol, in which the *apo*-base is less readily soluble, or of sodium hydroxide solution, in which ψ-codeine is insoluble.

ψ-*apo*Codeine is not a direct product from codeine, but is formed from the ψ-codeine, and a better yield is obtained by heating ψ-codeine with oxalic acid. It crystallises from alcohol in brilliant plates containing 1EtOH and melting and decomposing at 100—110°. The *hydriodide*, $C_{18}H_{19}O_2N,HI$, is sparingly soluble, and crystallises from water in slender needles, m. p. 288° (decomp.). The *diacetyl* derivative crystallises from alcohol in glistening plates, m. p. 135°. J. J. S.

Transformation of Narcotine into Nornarceine. The Cinchona-toxines. PAUL RABE (*Ber.*, 1907, 40, 3280—3287. Compare this vol., i, 78).—The correctness of the formula for cinchonine has been further tested by comparing narcotine and cinchonine. Narcotine methiodide is converted into narceine by heating with alkalis (Roser, Abstr., 1888, 1316; Freund and Frankforter, Abstr., 1894, i, 58), a change analogous with that of cinchonine into methylcinchotoxine; in both cases, the ring opens, an alcoholic hydroxyl disappears, and a ketonic group is formed. Dilute acetic acid converts cinchonine into cinchotoxine, a keto-base (v. Miller and Rhode, Abstr., 1894, i, 432), and the present communication deals with the action of this acid on narcotine. When heated together for seventy-two hours at 105—110° and the product neutralised with sodium hydroxide, a mixture of four compounds is precipitated. Nornarceine and meconine are extracted from this mixture by normal sodium hydroxide at the ordinary temperature; carbon dioxide precipitates the nornarceine, and the meconine is obtained from the filtrate by addition of mineral acid. The residue insoluble in alkali consists of unaltered narcotine and gnoscopine (Smith, Abstr., 1878, 987), which are separated by using alcohol, gnoscopine being sparingly soluble. Addition of sodium hydroxide to the neutral solution precipitates cotarnine. Forty-three grams of narcotine gave 9 grams of narcotine, 4 gnoscopine (m. p. 228—233°), 6 nornarceine, 9 cotarnine, and 7 meconine.



Nornarceine, obtained from its aqueous solution, crystallises in felted needles with $3H_2O$ and has no definite m. p. (between 205—222° decomp.). When heated at 105° the water is driven off, and the extremely hygroscopic substance then decomposes at 147°. If, however, the substance is recrystallised from alcohol, another modification is obtained, m. p. 229° (decomp.), forming prismatic crystals. This may be reconverted into the other isomeride by recrystallisation from water. The *hydrochloride*, $C_{22}H_{25}O_8N{\cdot}HCl{\cdot}H_2O$, has m. p. 144°. Hydroxylamine hydrochloride yields an *oximinoanhydride hydrochloride*, $C_{22}H_{25}O_7N_2Cl$, which crystallises with 1 mol. of ethyl alcohol, m. p. 138°; the *oxime*, $C_{22}H_{26}O_7N_2$, obtained by treating the above hydrochloride with the calculated amount of silver carbonate, crystallises in rhombic leaflets, m. p. 171°, and is not converted into anhydride at 108° in contradistinction from narceineoxime (Freund and Frankforter, *loc. cit.*). A methyl-alcoholic solution of nornarceine (1 mol.), 2 mols. of methyl sulphate, and excess of methyl iodide yields Freund's narceinium methiodide methyl ester (this vol., i, 235).

Nornarceine undergoes no change on heating with dilute acetic acid, whereas gnoscopine is converted into cotarnine, meconine, and nornarceine; the conclusion is therefore drawn that gnoscopine is an intermediate product in the reaction. As gnoscopine is inactive, racemisation must have occurred. W. R.

Tetrahydropyridine Bases. WILHELM KOENIGS, CARL BERNHART, and JOS. IBELE (*Ber.*, 1907, **40**, 3199—3210. Compare Abstr., 1905, i, 824; 1906, i, 36).—Pyridine bases, having an ethyl group in position 3, yield a not inconsiderable amount of the tetrahydro-base by reduction with sodium and alcohol.

The basic reduction products of 3-ethylpyridine are converted into the hydrobromides and the salts treated with bromine in cold chloroform solution, whereby the tetrahydro-base is isolated to the extent of 10—11% in the form of *dibromo-3-ethylhexahydropyridine hydrobromide*, $C_7H_{13}NBr_2,HBr$, m. p. 173° (decomp.); the *nitroso*-derivative,

$$C_7H_{12}ON_2Br_2,$$

has m. p. 90—91°, and responds only faintly to Liebermann's test. An isomeric 3-ethyltetrahydropyridine is formed in very small amount in the preceding reduction, and is isolated as the *dibromohydrobromide*, $C_7H_{13}NBr_2,HBr$, m. p. 195° (decomp.), which yields an oily *nitroso*-compound. 3-*Ethyltetrahydropyridine*, b. p. 157—159°/724·5 mm., obtained by treating the first-mentioned dibromo-3-ethylhexahydropyridine with zinc dust and dilute sulphuric acid, is a colourless oil with the odour of piperidine and decolorises acidified permanganate; the *hydrogen tartrate* has m. p. 134°; the *platinichloride*, m. p. 164—165° (decomp.); the *aurichloride*, m. p. 89°, and the *picrate*, m. p. 123—125°.

s-Trimethylpyridine yields by reduction with sodium and alcohol about 2% of the tetrahydro-base, which is isolated in the form of the *dibromonitrosoamine*, m. p. 146° (decomp.), the main product being *s*-trimethylpiperidine, which forms two isomeric hydrobromides having m. p. 204—209° and >270° respectively.

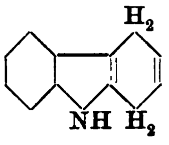
Tetrahydroaldehydecollidine (2-methyl-5-ethyltetrahydropyridine) is not attacked by sodium and alcohol, but is reduced to copellidine by hydriodic acid (D 1·96) and red phosphorus at 220°.

2-Methyl-5-ethylpyridine is regenerated from 2-methyl-5-ethyltetrahydropyridine dibromide hydrobromide by heating it to its melting point, by warming on the water-bath with 50% acetic acid and silver acetate, or by boiling its solution in glacial acetic acid with anhydrous sodium acetate with or without bromine. The hydrobromide is also decomposed by the prolonged boiling of its aqueous solution, yielding a *dihydroxy-2-methyl-5-ethyltetrahydropyridine*, $C_8H_{17}O_2N$, m. p. 155°, the *hydrochloride* of which has m. p. 200—201°, and the *hydrobromide*, 180—181°; the *picrate*, *platinichloride*, and *aurichloride* are very soluble in water.

1-*β*-*Naphthalenesulphonyl-2-methyl-5-ethyltetrahydropyridine*, $C_{18}H_{21}O_2NS$, has m. p. 71—72°. C. S.

Some New Bromo-derivatives of Pyridine. LÉONCE BARTHE (*Compt. rend.*, 1907, **145**, 75—77).—When a mixture of pyridine and sodium hypobromite is gradually treated with hydrochloric acid in amount sufficient to liberate all the bromine and the product heated in a reflux apparatus, a golden-yellow solution is obtained. From the latter, *pyridine hydrobromide*, C_5NH_5,HBr, is isolated in white, deliquescent crystals, m. p. 25°, which can be kept in a desiccator containing calcium chloride, but dissociate in one containing sulphuric acid. The aqueous solution has an acid reaction. By treating a mixture of pyridine and excess of hypobromite, heated on a water-bath, with hydrochloric acid, or by adding bromine to the yellow solution obtained above, a *tribromopyridine*, $C_5NH_3Br_3$, is formed in red needles, m. p. 89—90°, b. p. 230°, which thus differs from Willstätter's tribromopyridine, m. p. 167—168°. When pyridine is treated with bromine and the excess evaporated on a water-bath, a gummy residue is obtained from which, after some months, colourless, slightly deliquescent crystals of *bromopyridine*, C_5NH_5Br, m. p. 212° (decomp.), are isolated. The latter is not identical with either of the bromopyridines described by Hofmann, Ciamician, and Dennstedt (Abstr., 1882, 1214), or Ciamician and Silber (*Ber.*, 1886, **18**, 721). E. H.

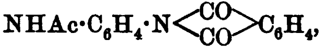
Dihydrocarbazole. JULIUS SCHMIDT and RICHARD SCHALL (*Ber.*, 1907, **40**, 3225—3230).—*Dihydrocarbazole*, $C_{12}H_{11}N$, obtained among the products of the reduction of carbazole by sodium and boiling amyl alcohol, separates from toluene in colourless leaflets which still contain traces of carbazole. It has m. p. 228—229° and b. p. 337—338°, possesses feebly basic properties, and is easily reconverted into carbazole. In the light of Thiele's theory, the two additional hydrogen atoms are assumed to occupy positions 1 and 4.



The *nitroso*-derivative, m. p. 72—73° (decomp.), forms golden-yellow needles and is very unstable. The *picrate* has m. p. 179—180°.

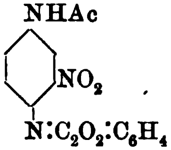
Dihydrocarbazole is easily reduced to tetrahydrocarbazole by sodium and amyl alcohol, and to the hexahydro-base by hydriodic acid and phosphorus at 150—160°. C. S.

Monosubstitution Products of Diacylated *p*-Phenylenediamines with Different Acid Radicles. ARNOLD CHAZEL (*Ber.*, 1907, 40, 3177—3185).—The influence of two fatty acylamino-groups on the position assumed by a negative-substituting group on introduction into the benzene nucleus was studied by Koller (Abstr., 1903, i, 281). The present paper is a similar study of the influence of two acylamino-groups, one of which contains a fatty, the other an aromatic, acid radicle. It is found that, on nitration in concentrated sulphuric acid solution, p-*acetylaminophenylphthalimide*,

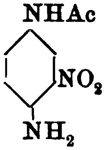


$$NHAc\cdot C_6H_4\cdot N{<}{\substack{CO\\CO}}{>}C_6H_4,$$

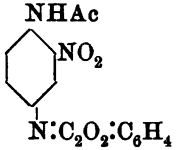
yields o-*nitro*-p-*acetylaminophenylphthalimide*, I, which on partial hydrolysis with ammonia forms *m*-nitro-*p*-aminoacetanilide, II, but on nitration with fuming nitric acid yields m-*nitro*-p-*acetylaminophenylphthalimide*, III, which on hydrolysis forms o-*nitro*-p-*aminoacetanilide*, IV.



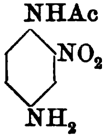
(I.)



(II.)



(III.)



(IV.)

p-*Acetylaminophenylphthalimide*, $C_{16}H_{12}O_3N_2$, formed together with the corresponding *phthalamic acid* by the condensation of *p*-aminoacetanilide with phthalic anhydride in boiling aqueous solution, crystallises in white needles, m. p. above 270°, and is readily soluble in alcohol, but insoluble in alkalis.

o-*Nitro*-p-*acetylaminophenylphthalimide*, $C_{16}H_{11}O_5N_3$, crystallises in yellow needles, m. p. 246°.

m-*Nitro*-p-*acetylaminophenylphthalimide*, $C_{16}H_{11}O_5N_3$, crystallises in yellow needles, m. p. 248·5—249°.

o-*Nitro*-p-*aminoacetanilide*, $C_8H_9O_3N_3$, crystallises in dark red needles, m. p. 162·5°.

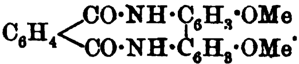
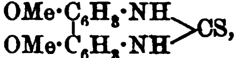
p-*Acetylaminophenylphthalamic acid*,

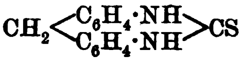
$$NHAc\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H,$$

is a white, crystalline substance, m. p. above 270°, and is insoluble in alcohol, but dissolves in alkali carbonates; the *barium* salt, $C_{32}H_{16}O_8N_4Ba$, forms reddish-white needles. On nitration in concentrated sulphuric acid solution, the acid yields o-*nitro*-p-*acetyl-*

aminophenylphthalamic acid, $C_{16}H_{13}O_6N_3$, which crystallises in orange-yellow needles, m. p. 177°, and on hydrolysis forms *m*-nitro-*p*-aminoacetanilide. *Dinitro*-p-*acetylaminophenylphthalamic acid*, $C_{16}H_{12}O_8N_4$, prepared by nitration of the acid with fuming nitric acid, crystallises in yellow needles commencing to decompose at 180°. G. Y.

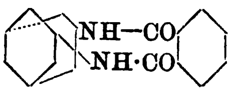
Stereochemical Conceptions of Polycyclic Compounds. II.

Felix Kaufler (*Ber.*, 1907, 40, 3250—3252. Compare this vol., i, 307, 776, and following abstracts).—The following evidence is brought forward in favour of the space formulæ of diphenyl and naphthalene (*loc. cit.*). Phthalyldianisidine is unimolecular and is represented by the formula  $C_6H_4<\begin{matrix}CO\cdot NH\cdot C_6H_3\cdot OMe\\ CO\cdot NH\cdot C_6H_3\cdot OMe\end{matrix}$. The proximity of the para-positions is also proved by the existence of 3 : 3′-dimethoxy-4 : 4′-diphenylthiocarbamide,  $\begin{matrix}OMe\cdot C_6H_3\cdot NH\\ OMe\cdot C_6H_3\cdot NH\end{matrix}>CS$, which is shown to be unimolecular by the ebullioscopic method in nitrobenzene.

4 : 4′-Diaminodiphenylmethane condenses with carbon disulphide to form diphenylmethanethiocarbamide,  $CH_2<\begin{matrix}C_6H_4\cdot NH\\ C_6H_4\cdot NH\end{matrix}>CS$; 4 : 4′-diaminodiphenylethane reacts similarly.

The influence of steric hindrance in 2 : 7-naphthylenediamine is seen in the fact that only one amino-group can be diazotised.

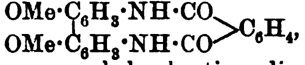
By a comparison of the physical properties and of the velocity of hydrolysis of the nitriles and of the methyl esters of 2 : 6- and 2 : 7-naphthalenedicarboxylic acids with those of the corresponding compounds of terephthalic and of *iso*phthalic acids, it is shown that the 2 : 6- and the 2 : 7-positions in naphthalene are analogous with the para- and meta-positions respectively in the benzene nucleus. This analogy is manifested, not only in the case of Willstätter and Parnas' 2 : 6-naphthaquinone, but also in the behaviour of dihydroxynaphthalenes to diazo-compounds; 2 : 7-dihydroxynaphthalene yields a disazo-compound, whilst the 2 : 6-compound forms substances of high molecular weight, probably dinaphthyl derivatives. This behaviour recalls that of resorcinol and of quinol under similar treatment.



The condensation of 2 : 7-naphthylenediamine and phthalic acid to form phthalylnaphthylenediamine is inexplicable by plane formulæ, and the author suggests that it is best represented by the annexed spacial formula. C. S.

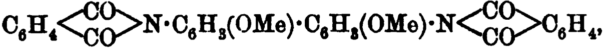
Ring Formation in Derivatives of Diphenyl, Diphenylmethane, and Diphenylethane.

Felix Kaufler and **H. Borel** (*Ber.*, 1907, 40, 3253—3256).—*Phthalyldianisidide*,



$$\begin{matrix}OMe\cdot C_6H_3\cdot NH\cdot CO\\ OMe\cdot C_6H_3\cdot NH\cdot CO\end{matrix}>C_6H_4,$$

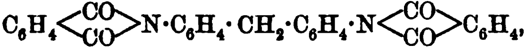
m. p. 216—217°, is prepared by heating dianisidine and phthalic anhydride with water for fourteen to sixteen hours. If the two substances are heated at 200—250° in the absence of water, yellow crystals of *diphthalyldianisidide*,



$$C_6H_4{<}\substack{CO\\CO}{>}N\cdot C_6H_3(OMe)\cdot C_6H_3(OMe)\cdot N{<}\substack{CO\\CO}{>}C_6H_4,$$

are obtained, m. p. above 330°.

Diphthalyldiaminodiphenylmethane,



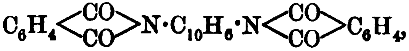
$$C_6H_4{<}\substack{CO\\CO}{>}N\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot N{<}\substack{CO\\CO}{>}C_6H_4,$$

m. p. 324°, prepared by boiling phthalic anhydride and 4 : 4′-diaminodiphenylmethane with water for ten to twelve hours, forms yellow leaflets. When 4 : 4′-diaminodiphenylmethane is heated with alcohol and carbon disulphide for eighteen to twenty hours, *diphenylmethanethiocarbamide*, $CH_2{<}\substack{C_6H_4\cdot NH\\C_6H_4\cdot NH}{>}CS$, m. p. 205° (decomp.), is obtained, which separates from dimethylaniline in yellowish-grey crusts, and is insoluble in acids.

4 : 4′-Diaminodiphenylethane yields similar compounds. *Diphthalyldiaminodiphenylethane*, $C_{30}H_{20}O_4N_2$, has m. p. above 330°, and *diphenylethanethiocarbamide*, $C_{15}H_{14}N_2S$, m. p. 272—273°. C. S.

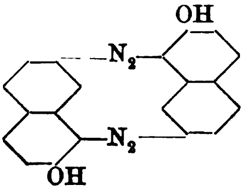
2 : 7-Derivatives of Naphthalene. FELIX KAUFLER and U. KARRER (*Ber.*, 1907, **40**, 3262—3269).—2 : 7-Naphthylenediamine is best diazotised in alcoholic solution by hydrobromic acid and amyl nitrite, whereby the *hydrobromide* of an *aminodiazonaphthalene bromide*, $C_{10}H_9N_3Br_2$, is precipitated in glistening, yellow needles, which explode by heating or in contact with concentrated nitric acid; it couples with β-naphthol in alkaline alcoholic solution to form 7-*aminonaphthalene*-2-*azo*-β-*naphthol*, $C_{20}H_{15}ON_3$, m. p. above 300°, which forms a yellowish-brown, microcrystalline powder. The hydrochloride of the corresponding diazo-chloride reacts with dimethylaniline to form 7-*aminonaphthalene*-2-*azodimethylaniline*, $C_{18}H_{18}N_7$, m. p. 259—260°, which separates from pyridine in glistening, reddish-brown leaflets.

Phthalyl-2 : 7-*naphthylenediamine*, $C_{10}H_6{<}\substack{NH\cdot CO\\NH\cdot CO}{>}C_6H_4$, m. p. 215°, is obtained by heating 2 : 7-naphthylenediamine and phthalic anhydride with water for two days; it separates from dimethylaniline in yellowish crusts, and is shown to be unimolecular by the ebullioscopic method with the same solvent, the molecular elevation of which is 50·8 experimentally, 49·4 by Nernst's formula, and 48·5 by Trouton's formula. *Diphthalyl*-2 : 7-*naphthylenediamine*,



$$C_6H_4{<}\substack{CO\\CO}{>}N\cdot C_{10}H_6\cdot N{<}\substack{CO\\CO}{>}C_6H_4,$$

m. p. 306°, obtained by heating phthalic anhydride and 2 : 7-naphthylenediamine at 250°, forms glistening, greenish-yellow leaflets.



7-Amino-2-naphthol is best diazotised by hydrochloric acid and amyl nitrite in alcoholic solution; the precipitated diazo-chloride and dimethylaniline yield 7-*hydroxynaphthalene*-2-*azodimethylaniline*, $C_{18}H_{17}ON_3$, which forms yellow solutions with alkalis and red solutions with acids. If the diazo-chloride is dissolved in a solution of sodium carbonate, a red *substance* is obtained, m. p. above 330°, which is shown by the ebullioscopic method in pyridine to have a molecular weight corresponding with the formula $C_{20}H_{12}O_2N_4$; it probably has the annexed constitution.

C. S.

Action of Diazo-Chlorides on γ-Chloroacetylacetic Esters.

G. Favrel (*Compt. rend.*, 1907, **145**, 194—196. Compare Abstr., 1902, i, 644).—The action of diazobenzene on ethyl γ-chloroacetylacetate yields the *γ-phenylhydrazone* of *ethyl-α-chlorobutane-βγ-dione-δ-carboxylate*, $CH_2Cl\cdot CO\cdot C(N_2HPh)\cdot CO_2Et$, which crystallises from alcohol in yellow needles, m. p. 92—93°. The prolonged action of diazobenzene chloride on this compound yields ethyl diphenylformazylformate, $CO_2Et\cdot C(N{:}NPh){:}N_2HPh$.

The γ-o-*tolylhydrazone* of *ethyl α-chlorobutane-βγ-dione-δ-carboxylate*, obtained by the action of diazo-*o*-toluene chloride on ethyl γ-chloroacetylacetate, forms slender, yellow needles, m. p. 121—122°, and is sparingly soluble in alcohol.

The γ-p-*tolylhydrazone* of *ethyl α-chlorobutane-βγ-dione-δ-carboxylate* is obtained as an orange-yellow, crystalline powder, m. p. 96—97°, soluble in alcohol.

Similarly, methyl γ-chloroacetylacetate yields:

$CH_2Cl\cdot CO\cdot C({:}N_2HPh)\cdot CO_2Me$,

yellow needles, m. p. 126—127°;

$CH_2Cl\cdot CO\cdot C[{:}N_2H\cdot C_6H_4Me(2)]\cdot CO_2Me$,

slender needles, m. p. 158—159°, and

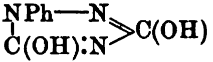
$CH_2Cl\cdot CO\cdot C[{:}N_2H\cdot C_6H_4Me(3)]\cdot CO_2Me$,

m. p. 139—140°.

T. H. P.

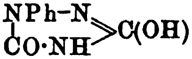
Constitution of Phenylurazole. III. Study of Tautomerism.

Salomon F. Acree (*Amer. Chem. J.*, 1907, **38**, 1—91. Compare Abstr., 1902, i, 242; 1903, i, 867; 1904, i, 270, 351, 453; this vol., i, 258).—In continuation of the work on the constitution of phenylurazole, the following five formulæ have been considered:



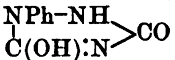
$\begin{array}{l}\mathrm{NPh{-}N}\\ \mathrm{C(OH){:}N}\end{array}\!>\mathrm{C(OH)}$

(I.)



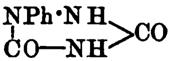
$\begin{array}{l}\mathrm{NPh{-}N}\\ \mathrm{CO\cdot NH}\end{array}\!>\mathrm{C(OH)}$

(II.)



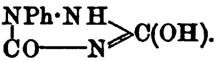
$\begin{array}{l}\mathrm{NPh{-}NH}\\ \mathrm{C(OH){:}N}\end{array}\!>\mathrm{CO}$

(III.)



$\begin{array}{l}\mathrm{NPh\cdot NH}\\ \mathrm{CO{-}NH}\end{array}\!>\mathrm{CO}$

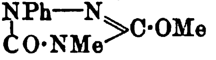
(IV.)



$\begin{array}{l}\mathrm{NPh\cdot NH}\\ \mathrm{CO{-}N}\end{array}\!>\mathrm{C(OH)}$.

(V.)

In order to study the equilibrium phenomena of the tautomeric amide groups, $\cdot NH\cdot CO\cdot$ and $\cdot N{:}C(OH)\cdot$, the action of diazomethane has been investigated. When a solution of phenylurazole in ether is treated with excess of diazomethane, 3-methoxy-1-phenyl-4-methylurazole (3-methoxy-5-keto-1-phenyl-4-methyl-4 : 5-dihydrotriazole),



$\begin{array}{l}\mathrm{NPh{-}N}\\ \mathrm{CO\cdot NMe}\end{array}\!>\mathrm{C\cdot OMe}$

(Abstr., 1903, i, 867), is formed together with traces of other dimethyl derivatives not yet identified. If, however, the phenylurazole is in excess, the chief product is 3-methoxy-1-phenylurazole (3-methoxy-5-keto-1-phenyl-4 : 5-dihydrotriazole), a small quantity (about 5%) of 1-phenyl-2-methylurazole being also formed.

These results indicate that there is equilibrium between the enolic and ketonic forms of the 2 : 3-amide group, the enolic form largely preponderating. When 3-methoxy-1-phenylurazole, 3-ethoxy-1-phenylurazole, 2-acetyl-1-phenylurazole, or 3-thio-1-phenylmethylurazole is treated with diazomethane, the corresponding 4-methyl derivatives are produced almost to the exclusion of the 5-methoxy-derivatives, whence it seems probable that the 4 : 5-amide group also exists in two tautomeric forms in equilibrium, but with the ketonic form in excess.

Both phenylurazole and 3-thio-1-phenylurazole are moderately strong acids and redden litmus. A study of the strength of the acid groups in phenylurazole has shown that the 2 : 3-amide group has an affinity constant $K = 0{\cdot}00001$ and the 4 : 5-amide group, $K = 0{\cdot}00000005$, which confirms the conclusion that the 2 : 3-amide group is enolic, whilst the 4 : 5-group is ketonic.

Although both phenylurazole and 3-thio-1-phenylurazole have two hydrogen atoms replaceable by metals, yet when treated with alkali in presence of phenolphthalein they behave as monobasic acids. If, however, the first hydrogen atom is replaced by an alkyl group, the resulting compound (for example, 3-methoxy-1-phenylurazole) also behaves as a monobasic acid, whence it is evident that, like many other dibasic acids, these urazoles ionise in steps. It is calculated that the ionisation of the 4 : 5-amide group is depressed by the 2 : 3-amide group, or its sodium salt, to 1/15 of its normal amount.

It is pointed out that the evidence afforded as to the constitution of the urazoles by their reactions with diazomethane is only qualitative, and it is shown by a consideration of the mass law that the relative amounts of two stable derivatives formed by the reaction of a tautomeric compound, existing in two forms in equilibrium, with another reagent depends on (1) the relative reactivity of the two tautomeric forms towards the reagent; (2) the ratio between the amounts of the two tautomeric forms when they are in constant equilibrium with each other, and (3) the rapidity of the change of the tautomeric forms into one another as the equilibrium between is disturbed. In some cases, the reaction may be complicated by the rearrangement of one or each of the tautomeric forms into the other or into some other product.

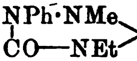
Various phases of the equilibrium conditions existing in a solution of a tautomeric acid or base, or their salts, have been studied, but for an account of these the original must be consulted.

A discussion is given of the conditions under which normal and abnormal hydrolysis of salts of tautomeric compounds can be determined, and it is shown that it is necessary to know (1) that equilibrium has been established in the solution of the tautomeric salt, or salts, when the hydrolysis is measured; (2) that equilibrium has been established in the solution of the tautomeric acid when its affinity constant is determined, and (3) that all the conditions of temperature, solvent, &c., are the same in (1) and (3).

The two modifications of α-ethyl phenylsemicarbazidecarboxylate (Wheeler and Beardsley, Abstr., 1902, i, 503), m. p. 172° and 154°, have the same molecular weight in aqueous solution. When the modification melting at 154° is heated above its m. p., it changes rapidly into the less fusible form. The change of one modification into the other by crystallisation from solvents depends on conditions of temperature, time, and the solvent employed. The solubility of the two forms in water is practically identical. It seems probable therefore that they are not chemical isomerides, but physical modifications.

When the potassium salt of phenylurazole is warmed with a solution of iodine, a soluble *compound* is formed, which is under investigation. By the action of alkyl haloids on potassium phenylurazole, 1-phenyl-2-alkylurazoles are formed together with very small quantities of 3-alkyloxy-1-phenylurazoles, whilst by their action on the silver salt, the latter compounds are obtained in comparatively large quantities.

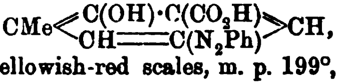
Dibenzoylphenylurazole has m. p. 178—180°. 2-*Benzoyl*-1-*phenyl*-4-*methylurazole*, m. p. 185°, is readily hydrolysed by concentrated hydrochloric acid. The *potassium* and *silver* salts of 3-ethoxy-1-phenylurazole are described.

1-*Phenyl*-2-*methyl*-4-*ethylurazole*,  $\left.\begin{matrix}NPh\cdot NMe\\ |\qquad\quad\\ CO\text{—}NEt\end{matrix}\right>CO$, m. p. 113°, is obtained by the action of ethyl iodide on the potassium salt of 1-phenyl-2-methylurazole.

[With FREDERICK LAIST.]—An account of the acetyl derivatives of phenylurazole (compare Abstr., 1905, i, 160). The *silver* derivative of 2-acetyl-1-phenylurazole is described. E. G.

Azo-derivatives of Certain Cresotic [Hydroxytoluic] Acids.

ERNESTO PUXEDDU and ENRICO MACCIONI (*Gazzetta*, 1907, **37**, i, 68—82).—The authors have prepared a number of azo-derivatives of *o*-, *m*-, and *p*-cresotic or homosalicylic acids [Me : CO_2H : OH = 1 : 3 : 2, 1 : 4 : 3, and 1 : 3 : 4 respectively]. All the compounds obtained are partially soluble in cold, and completely in hot, dilute alkali hydroxides, but are insoluble in water or dilute mineral acids. With nitric acid, they react violently, and with sulphuric acid they yield deep brown solutions. With phenylhydrazine, they give the corresponding amino-hydroxy-acids.

5-*Benzeneazo*-2-*hydroxy*-3-*toluic acid*,  $CMe\left<\begin{matrix}C(OH)\cdot C(CO_2H)\\ CH=\!=\!=C(N_2Ph)\end{matrix}\right>CH$, crystallises from alcohol in shining, yellowish-red scales, m. p. 199°, and in absolute ethereal solution gives with ferric chloride a wine-red coloration which turns brown when fresh ferric salt is added. The *sodium* salt forms prismatic, acicular crystals, and does not melt at 300°. Reduction of the acid with phenylhydrazine yields 5-amino-2-hydroxy-3-toluic acid, m. p. 267° (decomp.) (Nietzki and Ruppert, Abstr., 1891, 308, gave m. p. above 300°).

5-o-*Tolueneazo*-2-*hydroxy*-3-*toluic acid*, $C_{15}H_{14}O_3N_2$, separates from alcohol in microscopic, greenish-yellow crystals, m. p. 210° (decomp. at 212°).

5-p-*Tolueneazo*-2-*hydroxy*-3-*toluic acid*, $C_{15}H_{14}O_3N_2$, forms reddish-yellow crystals, m. p. 195°.

5-*β*-*Naphthaleneazo*-2-*hydroxy*-3-*toluic acid*, $C_{18}H_{14}O_3N_2$, forms dark brown, microscopic, mammillary masses, m. p. 229°.

6-*Benzeneazo*-3-*hydroxy*-4-*toluic acid*, $C_{14}H_{12}O_3N_2$, crystallises from alcohol in dark yellow, silky, prismatic needles, m. p. 216°. The *sodium* salt, $C_{14}H_{11}O_3N_2Na$, forms prismatic needles, not melting at 300°.

6-o-*Tolueneazo*-3-*hydroxy*-4-*toluic acid*, $C_{15}H_{14}O_3N_2$, is obtained as a grey, faintly yellow powder, m. p. 212°.

6-p-*Tolueneazo*-3-*hydroxy*-4-*toluic acid*, $C_{15}H_{14}O_3N_2$, crystallises from alcohol in twinned or curved, brick-red needles, m. p. 225°.

6-β-*Naphthaleneazo*-3-*hydroxy*-4-*toluic acid* is deposited from alcohol as a greenish-yellow, amorphous powder, m. p. 237°.

When 4-hydroxy-3-toluic acid is treated with diazo-salts, the corresponding azo-compound is not obtained, but carbon dioxide is eliminated and mono- and bisazo-*p*-cresols are formed.

Bisbenzeneazo-p-*cresol*, $C_{19}H_{16}ON_4$ [$Me : OH : (N_2Ph)_2 = 1 : 4 : 3 : 5$?], crystallises from alcohol in minute, dark red, acicular prisms, m. p. 180°, and dissolves in dilute alkali hydroxide solution forming a reddish-violet liquid. T. H. P.

Peri-derivatives of Naphthalene. FELIX KAUFLER and E. BRÄUER (*Ber.*, 1907, 40, 3269—3276).—5-*Nitro*-1-*naphthol*, m. p. 165°, is obtained in 30% yield by adding a solution of 5-nitro-1-diazonaphthalene sulphate to boiling 25% sulphuric acid; the *acetate* has m. p. 114°, and the *benzoate*, 109°. When the solution of the diazo-sulphate is kept at the ordinary temperature for three weeks, 5-nitro-4-nitroso-1-naphthol is formed, the *acetate* of which has m. p. 136°.

The reaction between *p*-nitrodiazobenzene chloride and 5-nitro-1-naphthol, dissolved in the calculated quantity of 10% sodium hydroxide, results in the formation of p-*nitrobenzene*-4-*azo*-5-*nitro*-1-*naphthol*, decomposing at 252—260°, p-*nitrobenzene*-2-*azo*-5-*nitro*-1-*naphthol*, m. p. 210°, and the *bisazo*-compound, m. p. 265°, which are separated by means of their different solubilities in toluene or in dilute sodium hydroxide; the bisazo-compound is also formed by treating a cold alcoholic solution of the *p*-hydroxyazo-compound with excess of sodium acetate and *p*-nitrodiazobenzene chloride.

2 : 7-Dihydroxynaphthalene reacts with *p*-nitrodiazobenzene chloride in alkaline solution to form a mixture of the *monoazo*- and the *bisazo*-compound, which is separated by means of the greater solubility of the former in toluene. It decomposes at 280—285°, separates from toluene in glistening, reddish-brown leaflets, and develops a violet coloration with sulphuric acid. The bisazo-compound decomposes above 300°, and gives a brownish-red coloration with sulphuric acid.

2 : 7-Dihydroxynaphthalene, dissolved in glacial acetic acid and treated with sodium nitrite, yields a *mononitroso*-compound, $C_{10}H_7O_3N$, decomposing at 230—240°; by nitration with nitric acid, D 1·4, in the same solvent, 2 : 7-dihydroxynaphthalene yields 1 : 8-*dinitro*-2 : 7-*dihydroxynaphthalene*, which forms yellow crystals, decomposing at 250°.

By the reaction between 2 : 6-dihydroxynaphthalene and diazobenzene chloride in alkaline solution, the *bisazo*-compound, $C_{22}H_{16}O_2N_4$, is precipitated; it crystallises in red needles, m. p. above 290°.

C. S.

Trisbenzeneazophenol. GUSTAV HELLER and OTTO NÖTZEL (*J. pr. Chem.*, 1907, [ii], 76, 58—61. Compare Vignon, Abstr., 1904, i, 699; Grandmougin and Freimann, this vol., i, 664).—Having obtained trisbenzeneazophenol in the course of an investigation to be described later, the authors have confirmed its constitution by reduction with stannous chloride and hydrochloric acid and benzoylation of the stannichloride so obtained by the action of benzoyl chloride in pyridine solution. The product is identical with the tetrabenzoyl-2 : 4 : 6-triaminophenol formed from picric acid by reduction and benzoylation in the same manner. Trisbenzeneazophenol is formed also by the action of diazobenzene chloride on bisbenzeneazophenol in alkaline solution. The *benzoate*, $C_{31}H_{22}O_2N_6$, crystallises in needles, m. p. 142°. The *sulphonic acid*, prepared by heating trisbenzeneazophenol with sulphuric acid containing 20% of anhydride, is readily soluble in water and dyes wool a weak red in an acid bath.

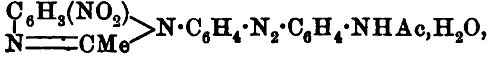
In view of the work of Goldschmidt and Löw-Beer (Abstr., 1905, i, 389), Willstätter and Veraguth (this vol., i, 453), and Auwers (*ibid.*, i, 554), trisbenzeneazophenol and its acyl derivatives are considered to be hydroxyazobenzene and not quinonehydrazone compounds. G. Y.

2 : 4 : 6-Trisbenzeneazoresorcinol. WILLIAM R. ORNDORFF and B. J. RAY (*Ber.*, 1907, 40, 3211—3214).—2 : 4 : 6-*Trisbenzeneazoresorcinol*, $C_6H(OH)_2(N_2Ph)_3$, m. p. 254°, prepared from diazobenzene chloride (3 mols.) and resorcinol in alkaline solution, forms microcrystalline, brown needles. The *diacetate*, $C_6H(OAc)_2(N_2Ph)_3$, separates from ethyl acetate and alcohol in orange-yellow needles, m. p. 201°, and from ether in red, prismatic crystals, m. p. 203°, which by recrystallisation from alcohol change into the orange-yellow needles. The constitution of the azo-compound is determined by its preparation from 4 : 6-bisbenzeneazoresorcinol and 2 : 4-bisbenzeneazoresorcinol. C. S.

Derivatives of *m*-Aminobenzene-*m*-azodiphenylamine. KURT BRAND (*Ber.*, 1907, 40, 3335—3340).—Chloro-2 : 4-dinitrobenzene readily reacts with a boiling alcoholic solution of *m*-azoaniline in the presence of sodium acetate, yielding 2 : 4-*dinitrophenyl*-m-*azoaniline*, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH_2$, together with s-2 : 4 : 2′ : 4′-*tetranitrodiphenyl*-m-*azoaniline*, $N_2[C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2]_2$. 2 : 4-Dinitrophenyl-*m*-azoaniline crystallises from ethyl acetate in glistening, red needles, m. p. 187—188°, and dissolves in alcoholic sodium or potassium hydroxide, yielding intense, deep red solutions. The *acetyl* derivative, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NHAc$, separates from glacial acetic acid in orange-yellow crystals, m. p. 233°. When reduced with an aqueous alcoholic solution of sodium hydrogen sulphide at 60—70°, the dinitro-compound yields 4-*nitro*-2-*aminophenyl*-m-*azoaniline*,

$$NO_2\cdot C_6H_3(NH_2)\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NH_2,$$

which crystallises from dilute alcohol in slender, pale red needles, m. p. 176—177°. It yields yellow salts, the solutions of which turn red when kept or when heated. When boiled with acetic acid and acetic anhydride, the nitroamino-compound yields *5-nitro*-1-m-*acetanilino*-m-*azophenyl-2-methylbenziminazole*,

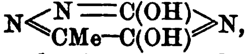


$$\left.\begin{array}{l}C_6H_3(NO_2)\\ N{=\!=}CMe\end{array}\right> N\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NHAc,H_2O,$$

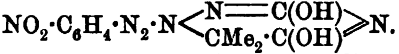
which crystallises from 96% alcohol in brilliant, glistening, yellowish-red prisms, melting at 148° with loss of water. When hydrolysed with sulphuric acid, it yields *5-nitro*-1-m-*anilino*-m-*azophenyl*-2-*methylbenziminazole*, $C_{20}H_{16}O_2N_6$, which crystallises in glistening, orange-yellow prisms, m. p. 175—176°.

Tetranitrodiphenyl-*m*-azoaniline may also be obtained by the condensation of 2 : 4-dinitrophenylazoaniline with chloro-2 : 4-dinitrobenzene. It crystallises from pyridine in glistening, golden-yellow needles, m. p. 285^{c}. J. J. S.

I. Diazoamino-compounds from Semicarbazino-fatty Acids. II. Chemical Behaviour of the Derivatives of Carbamidoazo-*iso*butyric Acid. JAMES R. BAILEY and LOUIS KNOX (*J. Amer. Chem. Soc.*, 1907, **29**, 881—892).—It has been shown previously that semicarbazino-fatty acids react with acid chlorides (Abstr., 1900, i, 528) and with thiocarbimides (Abstr., 1904, i, 826) in the same manner as do secondary amines. The present paper is an account of an investigation into the action of diazo-salts on semicarbazino-fatty acids. Whilst aromatic diazoamino-compounds, which do not contain the semicarbazide grouping, are formed by the action of diazo-salts on semicarbazide, or in some cases on semicarbazino-acids, it is possible in most cases with the semicarbazino-acids to obtain diazoamino-compounds in which the diazo-group is coupled directly with the α-nitrogen atom of the semicarbazide. Thus diazobenzene chloride and ethyl semicarbazinopropionate form *ethyl carbamidophenyldiazoaminopropionate*, $NH_2\cdot CO\cdot NH\cdot N(N_2Ph)\cdot CHMe\cdot CO_2Et$. Such substances do not give the general reactions characteristic of the diazoamino-compounds. They differ from each other in their behaviour towards alcoholic potassium hydroxide; whilst *ethyl carbamido*-m-*nitrophenyldiazoaminopropionate* yields 3 : 5-dihydroxy-6-methyl-1 : 2 : 4-triazine,



$N\left<\begin{array}{l}N{=\!=}C(OH)\\ CMe{-}C(OH)\end{array}\right>N$, nitrobenzene, nitrogen, and alcohol, *ethyl carbamido*-m-*nitrophenyldiazoamino*iso*butyrate* forms 1-m-*nitrophenylazo*-3 : 5-*dihydroxy*-6 : 6-*dimethyl*-1 : 6-*dihydro*-1 : 2 : 4-*triazine*,



$$NO_2\cdot C_6H_4\cdot N_2\cdot N\left<\begin{array}{l}N{=\!=}C(OH)\\ CMe_2\cdot C(OH)\end{array}\right>N.$$

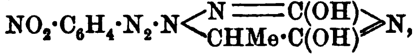
Attempts to prepare 3-hydroxy-5-keto-6 : 6-dimethyl-5 : 6-dihydro-1 : 2 : 4-triazine by this reaction and by other methods were unsuccessful.

Carbamidoazo*iso*butyric acid and the corresponding ketotriazine decompose at the moment of formation with loss of 1 mol. of nitrogen, whilst the *ethyl* ester decomposes a few degrees above its melting point, confirming Thiele and Heuser's observation (Abstr., 1896, i, 340) that azo-compounds of the aliphatic series are, as a rule, not very stable, and in many cases are incapable of existence.

Ethyl carbamidophenyldiazoaminopropionate, $C_{12}H_{17}O_3N_5$, crystallises in white, microscopic needles, m. p. 125° (exploding).

Ethyl carbamido-m-*nitrophenyldiazoaminopropionate*, $C_{12}H_{16}O_5N_6$, m. p. 146° (exploding), dissolves readily in cold bromine water, from which ammonia precipitates a brick-red *substance*, and on treatment with bromine in absolute alcoholic solution forms *m*-nitrodiazobenzeneimide. The *acid*, $C_{10}H_{12}O_5N_6$, has m. p. 128° (exploding); the *potassium* salt explodes at 184°; the *propyl* ester, $C_{13}H_{18}O_5N_6$, m. p. 149° (exploding); the *nitrile*, $C_{10}H_{13}O_3N_7$, forms a slightly yellow precipitate, m. p. 133° (exploding), and is converted by hydrogen chloride in absolute alcoholic solution into a white, crystalline *substance*, or by hydroxylamine into the *amidoxime*.

3 : 5-Dihydroxy-6-methyl-1 : 6-dihydro-1 : 2 : 4-triazine, m. p. 217° (209°: Thiele and Bailey, Abstr., 1899, i, 169), forms a potassium derivative, $C_4H_4O_2N_3K$, crystallising in white flakes, and couples with *m*-nitrodiazobenzene chloride, forming 1-m-*nitrophenylazo*-3 : 5-*dihydroxy*-6-*methyl*-1 : 6-*dihydro*-1 : 2 : 4-*triazine*,



$$NO_2\cdot C_6H_4\cdot N_2\cdot N<\begin{matrix}N=\!=\!=C(OH)\\ CHMe\cdot C(OH)\end{matrix}>N,$$

m. p. 121° (exploding).

Ethyl carbamido-m-*nitrophenyldiazoamino*iso*butyrate*, $C_{13}H_{18}O_5N_6$, crystallises from benzene and explodes at 133°.

1-m-*Nitrophenylazo*-3 : 5-*dihydroxy*-6 : 6-*dimethyl*-1 : 6-*dihydro*-1 : 2 : 4-*triazine*, $C_{11}H_{12}O_4N_6$, formed from the preceding ester, or by coupling the triazine with *m*-nitrodiazobenzene chloride, crystallises in light lemon flakes, m. p. 130° (exploding); the *potassium* salt crystallises in vermilion prisms and explodes at 166°.

Carbamido-m-*nitrophenyldiazoaminobenzene*,

$$NH_2\cdot CO\cdot NH\cdot NPh\cdot N_2\cdot C_6H_4\cdot NO_2,$$

formed by coupling phenylsemicarbazide with *m*-nitrodiazobenzene chloride, is obtained as a dark lemon-yellow substance, m. p. 104° (exploding).

m-Nitrodiazobenzene chloride is reduced by semicarbazide forming nitroaniline, which couples with unchanged diazo-compound, yielding *mm'*-dinitrodiazoaminobenzene. Semicarbazino-acids, which have no hydrogen atom attached to the α-nitrogen, as ethyl acetyl- and benzenesulphonyl-semicarbazinopropionates, do not couple with diazo-salts.

*Ethyl carbamidoazo*iso*butyrate*, $NH_2\cdot CO\cdot N{:}N\cdot CMe_2\cdot CO_2Et$, formed by oxidation of the semicarbazino-ester with bromine in aqueous solution, separates from benzene in yellow crystals, m. p. 83°, decomposes at 120°, and reacts violently with sodium ethoxide in alcoholic solution, evolving gas. The *methyl* ester is obtained as an oil, which when heated at 135—160° evolves gas and yields an *oil*, b. p. 232°/750 mm.

G. Y.

Physical Changes in the Conditions of Colloids. VI. The Coagulation of Acid Albumin by Heat. WOLFGANG PAULI (*Beitr. chem. Physiol. Path.*, 1907, **10**, 53—79. Compare Abstr., 1906, ii, 180).—The coagulation of albumin by heat is not reversible (compare Corin and Ansiaux, Abstr., 1891, 1521). **Experiments** have been made to determine the limiting concentrations of various potassium salts required to nullify the inhibiting action of a 0·005*N* solution of hydrogen chloride on the coagulation of a dialysed serum solution. The concentration required just to produce an opalescence in the boiled solution varied from 0·02*N* for potassium chloride to 0·002 for potassium citrate and acetate. The salts of the weakest acids appear to have the greatest coagulating effect. The action, however, is not due to a diminution of the concentration of the hydrogen ions, but is a direct action of the salt. Similar results were obtained when the same salts were used in the presence of acetic acid. An increase in the amount of acid required a considerable increase in the amount of neutral salt necessary to produce coagulation. A comparison of the action of different metallic chlorides in the presence of hydrochloric acid shows that the activity of the various salts increases in the order: calcium, magnesium, ammonium, potassium, sodium, lithium. The activity of nitrates in the presence of hydrochloric acid follows the order: barium, strontium, calcium, magnesium, potassium, but in both series the differences are not marked.

At the ordinary temperature, the thiocyanate ion has the most pronounced coagulating effect on acid albumin after forty-eight hours at the ordinary temperature; the effect of the thiocyanate ion is practically the same as that produced immediately after boiling. The various anions have not the same effect at the ordinary temperature as at the boiling point. At low temperatures, the increasing order of activity is acetate, sulphate, chloride, bromide, nitrate, thiocyanate, whereas at higher temperatures the order is nitrate, chloride, bromide, thiocyanate, sulphate, oxalate, acetate, citrate when the concentration of the acid is relatively low. If, however, the concentration of the acid is increased, the order at the higher temperature is the same as that at lower temperatures. For coagulation at both high and low temperatures, an increase in the amount of acid above a certain limit has practically no effect if the concentration of the salt remains constant. Similarly, for coagulation at high temperatures when the concentration of the acid is kept constant (0·005*N* hydrochloric acid) an increase in the concentration above a certain limit (about 0·2*N*) has practically no effect.

Coagulation produced in the cold is not increased by raising the temperature, but often disappears, leaving a clear liquid. J. J. S.

The Tryptic Digestion of Egg-albumin. Phœbus A. Levene and Wallace A. Beatty (*Bio-chem. Zeitsch.*, 1907, 4, 299—304. Compare Abstr., 1906, i, 469, 718).—Egg-albumin is extremely resistant to tryptic digestion, but, after four months in a 0·5% sodium carbonate solution of trypsin, a certain amount of hydrolytic decomposition had occurred. The products isolated were leucine, *iso*leucine, and tryptophan, together with a peptide which did not give the biuret reaction and, when hydrolysed, yielded lysine and glycine. A compound which belongs probably to the proteinochromogens was also obtained. J. J. S.

The Analysis of the Cleavage Products of Egg-albumin. Phœbus A. Levene and Wallace A. Beatty (*Bio-chem. Zeitsch.*, 1907, 4, 305—311. Compare Abderhalden and Pregl, Abstr., 1906, i, 53.)—Details are given for the isolation of the various products obtained by the hydrolysis of egg-albumin with concentrated hydrochloric acid. Fischer's esterification method was not used, and difficulties were met with in obtaining the leucine and tyrosine in a pure state. From 100 grams of material, the following products were obtained: alanine and glycine, 2·0; aminovaleric acid and leucine, 17·0; glutamic acid, 8·75; inactive *a*-proline, 0·5, and tyrosine, 1·25 grams. J. J. S.

Lysylglycine. Phœbus A. Levene and Wallace A. Beatty (*Proc. Amer. Sci. Biol. Chemists*, 1907, xxxix, *J. Biol. Chem.*, 3).—In the tryptic digestion of egg-albumin, a peptide was obtained, which on further cleavage yielded only lysine and glycine. It could not be crystallised. Fischer and Suzuki's peptides of the hexone bases also failed to crystallise. W. D. H.

Equilibrium between Proteids and Electrolytes. V. Completion of the Equilibrium Surfaces in the System, Globulin, Magnesium Sulphate, and Water. V. Scaffidi (*Zeitsch. physiol. Chem.*, 1907, 52, 42—53. Compare Abstr., 1904, i, 355; 1905, ii, 512; 1906, i, 912).—The four following curves have been determined for the system, globulin, magnesium sulphate, and water. 1. Isotherm at 55°. 2. Isotherm at 70°. 3. Coagulation curve of globulin. 4. Freezing point curve of the liquid phase.

At 55°, even after filtration, the solutions are opalescent. For all concentrations of magnesium sulphate, the solubility of globulin is less at 55° than at 40°, and for concentrations exceeding 17·9% the solubility diminishes rapidly until when the solution is saturated with the sulphate all the globulin is precipitated.

At 70°, the solutions become much more cloudy and cannot be filtered, so that another method of analysis must be used. At this temperature, a much less concentrated solution of magnesium sulphate is capable of completely precipitating the globulin.

The coagulation curve shows that the coagulating temperature has its minimum value when the concentration of the magnesium sulphate is small. It then rises rapidly with the concentration, afterwards more slowly, then falls again, and ultimately attains a practically constant value of 72° when the concentration of the sulphate is high.

These four curves, together with three of Galeotti's isotherms, are used for constructing equilibrium surfaces for the complete system.

J. J. S.

Deaminoglobulin. H. Lampel (*Monatsh.*, 1907, 28, 625—632).—It has been shown that neither deaminoglutin (Skraup, Abstr., 1906, i, 913) nor deaminocasein (Skraup and Hoernes, Abstr., 1906, i, 913) yield lysine on hydrolysis, although this compound is present in the hydrolysis products of glutin and casein. It is therefore probable that at least one of the amino-groups of the lysine residue is free in casein and glutin, and is hence attacked by the nitrous acid during the formation of the deamino-compound. The present investigation was carried out to see if the lysine residue in globulin is similarly destroyed during the treatment with nitrous acid, and such is found to be the case.

A quantitative estimation of the hexone bases, obtained by the hydrolysis of globulin from horses' blood, gave the following values: arginine, 2·8%, histidine, 3·4%, and lysine, 4·2%.

Deaminoglobulin is prepared by treating globulin in acetic acid solution with sodium nitrite; it is a light brown powder, insoluble in dilute acids and alkalis, but is turned intense red by the latter, which colour disappears on neutralisation; it does not give a decided Millon's or biuret reaction. On analysis, it is found to contain, roughly, the same quantities of hydrogen and sulphur, and slightly more carbon and nitrogen than globulin. When hydrolysed with sulphuric acid, it yields: arginine, 2·8%, histidine, 2·4%, lysine being absent from the product. W. H. G.

Iodothyrine. A. NÜRNBERG (*Beitr. chem. Physiol. Path.*, 1907, 10, 125—130. Compare Rohde, Abstr., 1905, i, 618).—Two specimens of iodothyrine, prepared from thyreoglobulin by Oswald's method, have been heated with water under varying conditions under pressure. The original preparations did not give the Adamkiewicz, Millon, or Ehrlich reaction; the one gave the biuret test, but not the other. After heating for several hours under a pressure of six atmospheres, the specimens gave the Millon reaction and to a certain extent the Ehrlich reaction.

The results are in harmony with the view that the iodothyrine contains iodotyrosine and iodotryptophan residues.

Iodothyrine also gives the Millon and Ehrlich reactions after treatment with sodium and alcohol. J. J. S.

Hydrolysis of Ichthylepidin and Fibrin. EMIL ABDERHALDEN and ARTHUR VOITINOVICI (*Zeitsch. physiol. Chem.*, 1907, 52, 368—374).—The results of hydrolysis of ichthylepidin (from the scales of the carp, *Cyprinus Carpio*) and of blood-fibrin were as follows:

	Ichthylepidin.	Fibrin.
Glycine	5·7%	2·0—3·0%
Alanine	3·1	3·6
Valine	—	1·0
Leucine	15·1	15·0
Proline	6·7	3·6
Phenylalanine	—	2·5
Aspartic acid	1·2	2·0
Glutamic acid	9·2	10·4—12·5
Serine	—	0·8
Tyrosine	1·0	3·5

The variations noted in fibrin indicate that it is not a single protein. W. D. H.

The Hydrolysis of Proteins by Means of Dilute Sulphuric Acid. PHŒBUS A. LEVENE and CARL L. ALSBERG (*Bio-chem. Zeitsch.*, 1907, 4, 312—315).—Gelatin, casein, and edestin have been heated with dilute sulphuric acid of different concentrations under pressure at temperatures between 140° and 170°. In each experiment, after hydrolysis, the total nitrogen, the nitrogen contained in the filtrate after half saturating with zinc sulphate, and also after complete saturation were estimated, and also the nitrogen contained in the filtrate after precipitation with 10% phosphotungstic acid. Gelatin behaves somewhat differently from the other proteins, the gelatoses being readily decomposed. With gelatin, also, the maximum yield of amino-acids corresponds with the disappearance of the biuret reaction. With the other acids, the substances which give the biuret reaction are completely decomposed before the maximum yield of amino-acids is attained. J. J. S.

Action of Sodium Hypobromite on Casein. ZDENKO H. SKRAUP and REINHOLD WITT (*Monatsh.*, 1907, 28, 605—624).—It is found that when casein, gelatin, egg-albumin, and globulin are treated with alkaline sodium hypobromite at the ordinary temperature, they give off roughly 20% of their total nitrogen as nitrogen, and, except in the case of globulin, the same quantity of nitrogen is evolved even after previous hydrolysis of the protein. Among the products formed by the action of sodium hypobromite on casein, were found histidine and lysine to about the same extent as obtained by the hydrolysis of casein, but no arginine, as was to be expected (compare Stuchetz, Abstr., 1906, i, 812). Several other amino-acids are also destroyed by the sodium hypobromite, since, although small quantities of leucine and active proline were isolated, the presence of glutamic acid, *r*-proline, aspartic acid, phenylalanine, glycine, and alanine could not be detected. An oil was also isolated, which, although an aldehyde and similar to benzaldehyde in properties, could not be definitely identified as this compound. Acetic, propionic, valeric, oxalic, and succinic acids were also identified. The formation of valeric acid by the oxidation of casein by sodium hypobromite is of great interest, for, since it cannot be derived from ordinary leucine, it shows that there is probably present in casein an isomeric, normal leucine. The investigation is being continued in this direction.

W. H. G.

Hydrolysis of Legumin from the Pea. THOMAS B. OSBORNE and SAMUEL H. CLAPP (*J. Biol. Chem.*, 1907, 3, 219—225).—The results of acid hydrolysis in parts per cent. are as follow: glycine, 0·38; alanine, 2·08; valine, not isolated; leucine, 8; proline, 3·22; phenylalanine, 3·75; aspartic acid, 5·3; glutamic acid, 13·8; serine, 0·53; cystine, not determined; tyrosine, 1·55; arginine, 10·12; lysine, 4·29; histidine, 2·42; ammonia, 1·99. This accounts for 57·43% of the protein. Tryptophan was present. W. D. H.

Azolitmin Compounds of Proteins. JACOB ROSENBLOOM and WILLIAM J. GIES (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxxix.—xl., *J. Biol. Chem.*, 3).—It is well known that mucoids are acid to litmus; pure moist mucoid mixed with blue litmus or azolitmin yields a product of raspberry-red colour. The colour is not removed by any washing process. It is turned blue by alkali; this blue is soluble in water. The view is put forward that the phenomena are not due to adsorption, but that a definite compound is formed. Nucleo-proteins are stated to behave in a similar way. W. D. H.

Oxidation of Oxyhæmoglobin. I. SZREYER (*Compt. rend.*, 1907, 145, 203—205).—By gradually adding hydrogen peroxide solution to a solution of crystallised oxyhæmoglobin, prepared from horses' blood, the author obtains an almost white, extremely hygroscopic, amorphous powder, which gives a red biuret reaction. In aqueous solution, it is not precipitated by concentrated mineral acids, and is not coagulated by heating. It is precipitated in colourless flocks by strong alcohols, neutral salts, potassium ferrocyanide, metaphosphoric acid, or the alkaloid reagents. Analysis gives the following percentage composition. Mineral matter, 3·36; iron, 0·47—0·49; carbon, 41·18—41·46; hydrogen, 6·2—6·39, and nitrogen, 13·89—14·16. T. H. P.

Hydrolysis of Spleen Nucleo-protein. JOHN A. MANDEL and PHŒBUS A. LEVENE (*Proc. Amer. Soc. Biol. Chemists*, 1907, xxiii—xxiv., *J. Biol. Chem.*, 3; *Bio-chem. Zeitsch.*, 1907, 5, 33—44).—Hydrolysis of the nucleo-protein of the spleen yielded in parts per cent. the following substances: glutamic acid, 25; leucine and valine, 6; glycine and alanine, 2; aspartic acid, 0·5; tyrosine, 1; lysine picrate, 7·5; arginine picrolonate, 2; histidine picrolonate, 0·5; adenine, 0·4; guanine, 0·6; cytosine, 0·7; thymine, 0·5; phenylalanine was present, and proline was not found. W. D. H.

Hydrolysis of Keratin from Horn and Wool. EMIL ABDERHALDEN and ARTHUR VOITINOVICI (*Zeitsch. physiol. Chem.*, 1907, 52, 348—367).—Keratins from the horns and wool of sheep were hydrolysed and the amounts of the various amino-acids are given in tables and compared with the results previously obtained from the keratin of hair and feathers, and from the horns of cattle. The results are in all cases different, and indicate that keratin is a mixture of proteins. W. D. H.

The Degradation of Keratin by Oxidation with Hydrogen Peroxide. FERDINAND BREINL and OSKAR BAUDISCH (*Zeitsch. physiol. Chem.*, 1907, 52, 159—169).—The products obtained by heating human hair, previously extracted with ether, with 30% hydrogen peroxide are sulphur, nitric and sulphuric acids; carbon dioxide, acetic, oxalic, and succinic acids; acetaldehyde, ammonia, and small amounts of amino-acids.

Glycine, alanine, leucine, aspartic acid, and cystine are oxidised when heated with 30% hydrogen peroxide, yielding ammonia, carbon dioxide, aldehydes, and organic acids. Tyrosine is not oxidised (compare Dakin, Abstr., 1906, ii, 105). J. J. S.

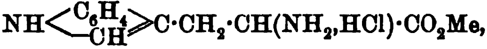
Whey Albumose. ERNST FULD (*Bio-chem. Zeitsch.*, 1907, 4, 488—499).—Numerous investigators have applied themselves to the problem of the origin and meaning of Hammarsten's whey-protein. The present experiments were carried out with solutions of pure caseinogen in lime water, which were neutralised with dilute phosphoric acid.

The solution was subjected to the action of rennet, and casein was precipitated by acetic acid; the filtrate gave no further precipitate on the addition of acetic acid, but gave the nitric reaction for albumoses. The name whey-albumose is therefore suggested. W. D. H.

Tryptophan and its Derivatives. EMIL ABDERHALDEN and MARTIN KEMPE (*Zeitsch. physiol. Chem.*, 1907, **52**, 207—218. Compare Hopkins and Cole, Abstr., 1902, i, 193; Neuberg and Popowsky, this vol., i, 253; Mayeda, *ibid.*, ii, 591).—Tryptophan prepared from casein by Hopkins and Cole's method has $[a]_D^{20^\circ}$ +6° in *N*/2 sodium hydroxide solution and +1·31° in *N*-hydrochloric acid solution. If the decomposition of the casein is allowed to proceed too long, the yield of tryptophan is small, and a by-product, $C_{11}H_{12}O_3N_2$, less soluble in water than tryptophan, is obtained. It crystallises in needles, turns yellow at 276°, and melts at 293° (corr.). When heated, it produces an odour of indole or scatole, but after boiling with concentrated hydrochloric acid, it yields an odour of quinoline when heated.

The *copper* salt of tryptophan, $(C_{11}H_{11}O_2N_2)_2Cu$, forms a pale blue precipitate, and when dry a greyish-blue powder; it is sparingly soluble in the usual solvents and in cold dilute mineral acids.

The *hydrochloride* of the methyl ester,



$$NH\left\langle\begin{matrix}C_6H_4\\ -CH\end{matrix}\right\rangle C\cdot CH_2\cdot CH(NH_2,HCl)\cdot CO_2Me,$$

crystallises from a mixture of methyl alcohol and ethyl acetate, has m. p. 214° (corr. decomp.), and dissolves readily in water or alcohol. The *methyl* ester, $C_{12}H_{14}O_2N_2$, crystallises from ether in large plates, m. p. 89·5° (corr.).

d-*Tryptophanphenylcarbimide*,

$$C_8NH_6\cdot CH_2\cdot CH(NH\cdot CO\cdot NHPh)\cdot CO_2H,$$

crystallises from dilute methyl alcohol in slender needles, m. p. 166° (corr.), and is remarkably sensitive to light, melting at 132° after exposure.

Sodium β-naphthalenesulpho-d-*tryptophan*,

$$C_8NH_6\cdot CH_2\cdot CH(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2Na,$$

crystallises from hot water in microscopic needles, m. p. 304° (corr.).

d-*Tryptophan chloride hydrochloride*,

$$C_8NH_6\cdot CH_2\cdot CH(NH_2,HCl)COCl,$$

melts and decomposes at 228° (corr.), and resembles the chlorides of amino-acids prepared by Fischer. J. J. S.

Equilibrium and Final Condition of Enzyme Reactions. HANS EULER (*Zeitsch. physiol. Chem.*, 1907, **52**, 146—158).—The question of equilibrium and final condition of typical enzyme reactions is discussed from the point of view that the enzyme forms compounds with the substrate and also with the products formed. It is pointed out that the numerical value for the end condition can only coincide with the "natural equilibrium" when the compounds enzyme-substrate and enzyme-reaction products are equally stable (compare Bodenstein and Dietz, *Zeitsch. Elektrochem.*, 1906, **12**, 605). It follows that the concentrations of a system in stable equilibrium will be altered by the addition of an enzyme. The question of ferments and anti-ferments is discussed. It is suggested that the injection of an enzyme destroys the normal relationship between the substrate and its decomposition products, and that the products produced by the injected ferment cause the secretion of an anti-ferment until the excess decomposition products are combined. The normal equilibrium between substrate and products is gradually re-established, but with a velocity which is small compared with that of the secretion of the anti-ferment, and thus an excess of free anti-ferment is found in the serum. If this is correct, it should follow that the injection into the organism of the decomposition products formed by the enzyme should produce the same effects as the injection of the enzyme. It should also follow that the anti-ferment action of a serum, obtained some time after the injection of the ferment, should continue to increase *in vitro*. J. J. S.

Enzyme Action. IX. The Enzymes of Yeast: Amygdalase. ROBERT J. CALDWELL and STEPHEN L. COURTAULD (*Proc. Roy. Soc.*, 1907, B, 79, 350—359).—The hydrolysis of amygdalin by yeast is due neither to maltase nor to invertase, but to a specific enzyme, *amygdalase*, not hitherto recognised.

Comparative experiments were made at 25° with solutions containing equivalent quantities of amygdalin, maltose, and methyl glucoside, and extracts of various yeasts which had been heated previously to different temperatures. The action on amygdalin and also on methyl-α-glucoside persisted after heating the extract to a temperature (50°) above that at which maltase is an active agent. At 60°, the hydrolysis of amygdalin and methyl-α-glucoside ceased, although the enzyme bringing about the inversion of sucrose was still active. The discovery of an *α-glucase* different from maltase is of interest. Whether there are two enzymes, one of which attacks amygdalin and the other methyl-α-glucoside, was not determined conclusively. There is some evidence to indicate that maltase can attack methyl-α-glucoside, and that amygdalase attacks both methyl-α-glucoside and amygdalin.

Amygdalase is equally well extracted from dried yeast at all temperatures from 15° to 45°. Whereas a low temperature extract affords a very small proportion of amygdalase, the quantity is increased by heating the extract for a short time at 45°; that is to say, the amygdalase is originally dissolved as part of a more complex protein or zymogen molecule, which is hydrolysed at the higher temperature.

Dextrose has an inhibitory effect on the hydrolysis of amygdalin by amygdalase, and, in this respect, maltose, lactose, and galactose are inert. G. S. W.

Enzyme Action. X. The Nature of Enzymes. HENRY E. ARMSTRONG and EDWARD F. ARMSTRONG (*Proc. Roy. Soc.*, 1907, B, 79, 360—365).—As the investigation is extended, the evidence becomes more and more convincing that the action which an enzyme exercises is specific, being limited to compounds of a particular type. Maltase, in the authors' opinion, is capable of hydrolysing α-glucosides alone, whilst emulsin hydrolyses β-glucosides. A table is given summarising the experiments in relation to sucroclasts and their inhibitants, showing that the enzyme and hydrolyte must be in complete correlation. The extraordinary activity of invertase makes it necessary to work with highly dilute solutions of the enzyme; the influence of small quantities of impurities is counteracted by means of amino-acids.

Nature of Enzymes.—The collected evidence demonstrates that during hydrolysis invertase extends its influence over the whole of the sucrose molecule. The question arises whether this is true of other biases. There are many indications which make it probable, at all events in the case of lactose, that what is true of sucrose and its correlative enzyme applies generally.

In the case of enzymes other than those which affect carbohydrates, the range of activity would appear, however, often to be greater than is ever manifested in the case of enzymes of the sucroclastic class. G. S. W.

Different Hydrolytic Actions Produced by a Single Enzyme. LUIGI MARINO and G. SERICANO (*Gazzetta*, 1907, **37**, i, 45—51).—The authors have prepared, from beer yeast, a sample of invertase which is capable of hydrolysing sucrose, but incapable of acting on α-methylglucoside, maltose, lactose, or salicin, and hence is quite free from maltase. This purified invertase resolves amygdalin into dextrose (1 mol.) and amygdonitrile glucoside, which, according to Fischer, is formed from amygdalin by the action of the maltase contained in beer yeast. The disaccharide of amygdalin must therefore be distinct from ordinary maltose. The fact that one and the same enzyme can effect the hydrolysis of disaccharides of different constitution is regarded by the authors as evidence supporting the view that special enzymes, such as trehalase, melibiase, melizitase, and gentiobiase, are non-existent. It is also pointed out that in no instance has a reversible action been observed with a single, well-defined enzyme. T. H. P.

Behaviour of Peroxydase towards Hydroxylamine, Hydrazine, and Hydrogen Cyanide. ALEXIS BACH (*Ber.*, 1907, **40**, 3185—3191. Compare this vol., i, 268).—The amounts of hydroxylamine hydrochloride, hydrazine sulphate, and potassium cyanide required for the complete destruction of peroxydase are of such magnitude that these substances cannot function as poisons, but must enter into stoichiometric reaction with the peroxydase. The amount of peroxydase destroyed by 2 mols. of hydroxylamine hydrochloride or potassium cyanide, or $\frac{1}{2}$ mol. of hydrazine sulphate, renders active 1 mol. of hydrogen peroxide. G. Y.

Rennet Action. M. VAN HERWERDEN (*Zeitsch. physiol. Chem.*, 1907, **52**, 184—206).—Whether the curdling action of rennet on caseinogen (casein) which results in the formation of casein (para-casein) is hydrolytic or not is still uncertain; the relation of whey-protein to the process is also a matter of speculation. It is, however, known that in curdling two processes occur, first, the action of the rennet, and then the precipitation of one or more of the products formed by calcium salts. The view now put forward is that the enzyme forms, from the labile caseinogen molecule, one with another constitution, and this main end-product is termed para-casein *A*. This is regarded as a complex containing para-casein *B* (which differs from *A* in being more readily precipitable by ammonium sulphate, and less so by alcohol) and a substance, *C*, which is not precipitated by acetic acid, and requires still more ammonium sulphate to precipitate it; it is soluble in water, gives a weak Adamkiewicz and a strong biuret reaction. By long continued action, a primary proteose appears, which is the beginning of a new phase characterised by further decomposition of the casein molecule.

Free hydrogen ions are not necessary for the coagulation of milk or of solutions of caseinogen which contain calcium. W. D. H.

Ferments and Anti-ferments. IV. MARTIN JACOBY (*Bio-chem. Zeitsch.*, 1907, **4**, 21—24).—In their adsorption phenomena (fibrin), the peptic and rennetic enzymes of Witte's rennet behave similarly. Horse serum manifests both an anti-peptic and an anti-rennetic action.

G. S. W.

Ferments and Anti-ferments. V. MARTIN JACOBY (*Bio-chem. Zeitsch.*, 1907, **4**, 471—483. Compare Abstr., this vol., ii, 108).—The presence of anti-ferments in blood-serum is confirmed; the absolute quantity of these is a more important factor than their concentration. Ferments are placed in the same group as toxins and the anti-ferments in the same category as anti-toxins; but, in addition to anti-ferments, the serum contains other substances which are dialysable and resist heat and hinder ferment activity. Rennin and pepsin can be separated from fibrin flocculi by alkalis, whilst the rennin—anti-rennin union is broken by acids. The view that the union of a ferment with the substrate is not identical with the union with the anti-ferment is thus confirmed.

Rennin and pepsin are soluble in alkalis, and trypsin is soluble in acids, whereas pepsin acts in an acid, and trypsin in an alkaline medium. It is possible in view of the analogies of inorganic chemistry and of what is known as to the physico-chemical behaviour of ferments, that the insoluble condition of the ferment is a critical moment in its activity. W. D. H.

Existence of a Tyrosinase in Wheat Bran. GABRIEL BERTRAND and MUTERMILCH (*Compt. rend.*, 1907, **144**, 1285—1288).—According to Mège-Mouriès (*ibid.*, 1856, **42**, 1122; 1857, **44**, 40, 449; 1859, **48**, 126) the colour of brown bread is caused by the action, during panification, of cerealin, a substance of a ferment nature contained in the bran. Boutroux (*ibid.*, 1895, **120**, 934) states that the bran contains laccase, and a substance of an undetermined nature on which the ferment acts. By macerating bran in water, precipitating the extract with alcohol, redissolving the precipitate in water, separating the insoluble portion by a centrifuge, reprecipitating with alcohol, and drying in a vacuum, the authors have obtained a substance soluble in water which does not contain laccase, since, when added to an aqueous solution of guaiacol, no tetraguaiacoquinone is produced (Abstr., 1903, i, 157). It contains an enzyme of the nature of a tyrosinase, as its aqueous solution, sterilised by filtration through a Chamberland filter, is not coloured by contact with atmospheric oxygen, but acquires first a rose, then a cherry-red and, finally, a dark brown colour when treated under aseptic conditions with a solution of tyrosine. The coloration is prevented by removal of all the oxygen by means of a mercury pump, or by heating the enzyme solution previously for five minutes on a water-bath at 100° (compare Abstr., 1896, ii, 571; 1897, ii, 117). The substance contains other enzymes, among which is Raciborsky's peroxydase (*Ber. Deut. bot. Ges.*, 1898, **16**, 119). Owing to the presence of the latter, the aqueous solution in the absence of oxygen, but in the presence of a little hydrogen peroxide, oxidises guaiacol to tetraguaiacoquinone and quinol to quinhydrone, and gives an intense blue coloration with the dye from guaiacum resin. E. H.

p-Aminophenylarsonic Acid. I. Paul Ehrlich and Alfred Bertheim (*Ber.*, 1907, **40**, 3292—3297).—Atoxyl is the sodium salt of the product obtained by Béchamp (*Compt. rend.*, 1863, **56**, 1172) by heating aniline arsenate at 190—200°, and described by him as the anilide. That it is not an anilide, but *p*-aminophenylarsonic acid, is shown. 1. It cannot be hydrolysed to aniline; 2. it contains a primary amino-group; 3. it possesses all the characteristic reactions described by Michaelis of arsonic acids, $R\cdot AsO(OH)_2$; 4. the arsenic acid radicle can be replaced by iodine, yielding *p*-iodoaniline. The action of heat is therefore comparable with the conversion of aniline sulphate into sulphanilic acid, and the name arsanilic acid is suggested for the substance.

Arsanilic acid, $NH_2\cdot C_6H_4\cdot AsO(OH)_2$, possessed weak basic properties; the *hydrochloride*, $C_6H_8O_3NAs,HCl$, is immediately hydrolysed by water; the *sodium* salt is neutral to test paper and crystallises with varying quantities of water. The *acetate*, $C_8H_{10}O_4NAs$, forms glistening, white leaflets, easily hydrolysed by hot alkalis or acids, does not react with naphthaquinonesulphonic acid, and forms a *sodium* salt. Arsanilic acid may be diazotised, and then forms with naphthylamine a red azo-dye, dissolving in cold sodium carbonate solution with a red colour. Sodium arsanilate, when heated with dilute sulphuric acid and potassium iodide, is converted into *p*-iodoaniline. W. R.

Organic Chemistry.

Hanoverian Petroleum. Felix B. Ahrens and Johannes Riemer (*Zeitsch. angew. Chem.*, 1907, **20**, 1557—1559).—The specimen of Wietze oil, D^{15} 0·941, examined, is viscous, blackish-brown, opaque even in thin layers, has only a slight odour of petroleum, gives a transient blue fluorescence with concentrated sulphuric acid, and has the specific viscosity 12·16 at 60°, the flash point 105°, and the ignition temperature 143°; its vapour tension is small, only 3·06% evaporating at the laboratory temperature in eight weeks. It contains 0·06—0·07% of mechanical impurities, and 0·86% of water, which, on evaporation, yields 25·27% of a residue consisting chiefly of sodium chloride together with small amounts of potassium and magnesium chlorides, and traces of calcium sulphate. The oil yields 15·8% of a distillate, b. p. 200—300°, D^{15} 0·86, n 1·462, $n-1/d$ 0·5384, which has the specific viscosity 1·44 at 20°, the flash point 47°, and the ignition temperature 69°. The distillation residue forms a black, viscous mass, D 0·9742, which, when "cracked," yields 75% of distillate and 18% of coke. The brown distillate, D 0·869, specific viscosity 1·51, flash point 45°, ignition temperature 64°, has a green fluorescence, and a strong, unpleasant odour; on fractionation, it yields 5% D 0·813, b. p. below 150°, 45% b. p. 150—300°, and 50% b. p. above 300°. The intermediate fraction, D 0·8292, has a specific viscosity 1·03, the flash point 34°, and the ignition temperature 49°. The fraction, b. p. above 300°, D 0·9092, has a specific viscosity 3·16, a flash point 161°, and the ignition temperature 187°.

When distilled/50 mm., the crude oil yields 85% of distillate and 10% of coke. The coke has an odour of hydrogen sulphide. The distillate, D 0·8753, specific viscosity 1·93, flash point 67°, ignition temperature 101°, yields on distillation 36·6% of illuminating oil, D 0·8315, specific viscosity 1·4, flash point 44°, ignition temperature 61°, and 63·4% of lubricating oil, D 0·9107, specific viscosity 4·14, flash point 153°, and ignition temperature 178°.

The examination of the various fractions shows that the oil consists chiefly of unsaturated and aromatic hydrocarbons, methane hydrocarbons, decane to pentadecane, and naphthenes, decanaphthene to tridecanaphthene, being present only in comparatively small amounts, and in the fractions boiling at the lower temperatures. The oil contains only 0·2879% of solid paraffins, and 1·03% of asphalt insoluble in light petroleum or 20·7% insoluble in ether-alcohol. G. Y.

Hexyl and Octyl Fluorides. Emanuele Paternò and Rosario Spallino (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 160—166).—*sec.-Hexyl fluoride* (*β-fluorohexane*), $CH_2Pr\cdot CHMeF$, prepared by the action of β-iodohexane on silver silicofluoride, has b. p. 82—86°, D^0 0·819, and $n_D^{26\cdot2}$ 1·3683.

n-*Octyl fluoride*, $C_8H_{15}F$, prepared from octyl iodide and silver silicofluoride, is a colourless liquid, b. p. 131—134°, D^0 0·798.

T. H. P.

Equilibria Involving the Addition of Ethylene. Julius Sand (*Zeitsch. physikal. Chem.*, 1907, 60, 237—251. Compare Sand and Breest, this vol., ii, 537).—A theoretical paper. The author shows how it should be possible, from electrochemical measurements in aqueous solutions of mercuric and mercurous compounds, and from the study of certain equilibria in solution, to calculate the changes of free energy involved in the reactions: $C_2H_4 + H_2O \rightleftarrows C_2H_5{\cdot}OH$; $C_2H_4 + H_2 \rightleftarrows C_2H_6$; $C_2H_4 \rightleftarrows C_2H_2 + H_2$.

J. C. P.

Comparative Oxidation of Di*iso*butylene by means of Potassium and Magnesium Permanganate. Nicolaus A. Prilerzaeff (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 769—771).—Magnesium permanganate oxidises di*iso*butylene less rapidly and thoroughly than potassium permanganate, and yields a less homogeneous product.

Z. K.

Bromomethylnitrolic Acid. Giacomo Ponzio and G. Charrier (*Gazzetta*, 1907, 37, ii, 99—104).—The authors have prepared bromo*iso*nitrosoacetone by the action of hydrobromic acid on acetylmethylnitrolic acid (compare Behrend and Schmitz, Abstr., 1894, i, 108; Behrend and Tryller, Abstr., 1895, i, 201) and have then treated it with nitric acid in order to obtain bromomethylnitrolic acid (compare Ponzio, this vol., i, 744). The latter is only formed together with oxalic acid and carbon tetrabromide in small proportion, the main product being dibromodinitromethane, which is probably derived from bromodinitromethane (compare Wolff, Abstr., 1893, i, 689). This reaction may, indeed, be used advantageously for the preparation either of dibromodinitromethane or of the potassium derivative of bromodinitromethane.

*Bromo*iso*nitrosoacetone*, $CBrAc{:}NOH$, crystallises from benzene in white prisms, m. p. 123—124°, and dissolves readily in alcohol, ether, or chloroform, and to a less extent in water.

Bromomethylnitrolic acid, $NO_2{\cdot}CBr{:}NOH$, crystallises from chloroform in faintly yellow needles, m. p. 93° (decomp.), is readily soluble in ether or alcohol and moderately so in benzene, is less stable than chloromethylnitrolic acid, and is soluble in cold water, which decomposes it according to the equation: $NO_2{\cdot}CBr{:}NOH = CO_2 + HBr + N_2O$. It dissolves in dilute alkali hydroxides, giving a blood-red liquid which rapidly becomes colourless, and is then found to contain only alkali carbonate and bromide in theoretical amount; the same reaction is produced by the alkaline earth hydroxides. It is moderately stable in presence of acids.

T. H. P.

Dehydration of Alcohol by Lime. Anton Kailan (*Monatsh.*, 1907, 28, 927—946).—This work was undertaken to obtain exact details as to the proportion of lime, and also the time, necessary for the dehydration of alcohol of 92—93% by weight, as these are not found in the literature. If 92—93% alcohol is boiled with lime in a reflux apparatus, the velocity of dehydration to 99·5% alcohol is independent of the amount of lime present if the value K/A, in which K is the weight of lime in kilograms and A is the volume of alcohol in litres, remains between 0·25 and 0·41; with $K/A > 0·4$, the velocity of the dehydration increases with the proportion of lime, at first rapidly, the velocity with $K/A = 0·5$ being thrice that with $K/A = 0·4$, but thereafter gradually more slowly. With $K/A > 0·5$, the value for the velocity constant k, as calculated by means of the equation for unimolecular reactions, remains fairly constant throughout each series, but with $K/A =$ or $< 0·4$, the value for k diminishes rapidly as the concentration of the alcohol increases above 99·5%. The loss of alcohol accompanying this method of dehydration increases rapidly with the proportion of lime employed; it is found most advantageous to add 0·55 kilogram of lime per litre of 92—93% alcohol, when 99·5% alcohol is obtained on boiling for three and a half hours, or 99·9% alcohol in about six hours. Dehydration takes place also at the ordinary temperature, but only slowly; with $K/A = 0·563$ at 20—22°, the dehydration is complete in about 575 hours. G. Y.

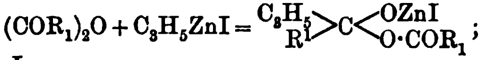
Mixtures of Trimethylcarbinol and Water. EMANUELE PATERNÒ and A. MIELI (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 153—160).—The curve representing the temperatures of equilibrium between the liquid and solid phases of mixtures of trimethylcarbinol and water exhibits two minima and a horizontal portion the mean position of which corresponds with a hydrate of the composition

$$C_4H_{10}O,2H_2O,$$

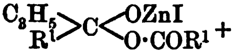
m. p. 0°. The density curves of the mixtures for temperatures between 0° and 70° have been determined and those for 0° and 24° confirm the existence of the above hydrate. Moreover, the viscosity at 24° is a maximum for a mixture of the constitution $C_4H_{10}O,2H_2O$.

T. H. P.

Action of Zinc Allyl Iodide on Anhydrides of Monobasic Acids. ALEXANDER M. SAYTZEFF [with F. PETROFF, N. MUSUROFF, S. CHOWANSKY, G. ANDRÉEFF, B. CHONOWSKY, and ANDREAS LUNJACK] (*J. pr. Chem.*, 1907, [ii], **76**, 98—104).—Several diallyl alkyl carbinols have been prepared by the method previously described (*J. Russ. Phys. Chem. Soc.*, 1906, **26**, 16), namely, by the action of zinc allyl iodide on the anhydrides of monobasic acids in ethereal solution, and their physical constants redetermined. In addition to the chief reaction:



$$(COR_1)_2O + C_3H_5ZnI = \begin{smallmatrix}C_3H_5\\ R^1\end{smallmatrix}\!>\!C\!<\!\begin{smallmatrix}OZnI\\ O\cdot COR_1\end{smallmatrix};$$



$\begin{smallmatrix}C_3H_5\\ R^1\end{smallmatrix}\!>\!C\!<\!\begin{smallmatrix}OZnI\\ O\cdot COR^1\end{smallmatrix} + C_3H_5ZnI = (C_3H_5)_2CR^1\cdot OZnI + COR^1\cdot OZnI$; the following reaction takes place to a certain extent: $(C_3H_5)_2CR^1\cdot OZnI + (COR^1)_2O = (C_3H_5)_2CR^1\cdot O\cdot COR^1 + COR^1\cdot OZnI$.

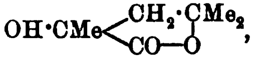
Methyldiallylcarbinol, b. p. 157—159°; D_0^0 0·87747, D_0^{20} 0·86134 (compare Sorokin, this Journ., 1877, 299). Ethyldiallylcarbinol, b. p. 175—176°/755·6 mm.; D_0^0 0·88603, D_0^{20} 0·86877 (compare Smirensky, Abstr., 1882, 488). Propyldiallylcarbinol, b. p. 192—194°;

D^{0}_{0} 0·87939, D^{20}_{0} 0·86286 (compare A. and P. Saytzeff, Abstr., 1879, 136). *iso*Propyldiallylcarbinol, b. p. 187—188°/759·8 mm.; D^{0}_{0} 0·88859, D^{20}_{0} 0·87133 (compare Rjabinin and Saytzeff, Abstr., 1879, 612).

W. H. G.

Preparation of Glycols from Keto-alcohols by the Action of Organo-magnesium Compounds. ADOLF FRANKE and MORITZ KOHN [and, in part, J. KOVAČEVIĆ and J. NEMLICH] (*Monatsh.*, 1907, 28, 997—1015. Compare this vol., i, 171).—The formation of β-glycols by the action of organo-magnesium compounds on β-hydroxy-aldehydes having been described previously, the investigation of the reaction has now been extended to the preparation of glycols by the action of organo-magnesium compounds on keto-alcohols.

When distilled with dilute sulphuric acid, βδ-dimethylpentane-βδ-diol (Abstr., 1905, i, 111; Zelinsky, Abstr., 1902, i, 593) yields *βδ-dimethyl-Δ^α-pentene-δ-ol*, $CH_2:CMe\cdot CH_2\cdot CMe_2\cdot OH$, b. p. 132°, which forms an *additive* compound with bromine. The *acetyl* derivative has b. p. 156—158°. Oxidation of the unsaturated alcohol with potassium permanganate leads to the formation of the *lactone*,

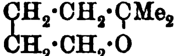


$$OH\cdot CMe<\begin{matrix}CH_2\cdot CMe_2\\ CO—O\end{matrix},$$

which crystallises in white leaflets, m. p. 64°, b. p. 248°/760 mm.

β-Methylpentane-βε-diol, $OH\cdot CMe_2\cdot[CH_2]_3\cdot OH$, prepared by the action of magnesium methyl iodide on acetopropyl alcohol (δ-keto-*n*-amyl alcohol), is obtained as a viscid, colourless oil, b. p. 118—120°/14 mm., or 218—219°/760 mm. When boiled with 10% sulphuric acid, the diol is converted into 2-*methyltetrahydrofuran*, $C_6H_{12}O$, which forms a colourless oil, b. p. 90—92°, has an odour resembling camphor, and remains unchanged when heated with water at 150°. Oxidation of the diol with potassium permanganate leads to the formation of acetone and a *lactone*, $C_6H_{10}O_2$, which is obtained as a mobile liquid, b. p. 200—202°, and has a characteristic odour resembling cinnamon. The corresponding *potassium* and *calcium*, $(C_6H_{11}O_3)_2Ca$, salts are described. A small amount of an acid product formed together with the lactone is probably malonic acid.

β-Methylhexane-βζ-diol, $OH\cdot CMe_2\cdot[CH_2]_4\cdot OH$, formed from acetobutyl alcohol (ε-keto-*n*-hexanol) and magnesium methyl iodide, is obtained as a colourless, viscid oil, b. p. 135°/19 mm., and on distillation under atmospheric pressure decomposes, forming an unsaturated *alcohol*, $C_7H_{14}O$, which is a colourless, mobile oil, b. p. 173°/760 mm., and yields an *additive* compound with bromine. When heated with sulphuric acid, the glycol yields *dimethylpentamethylene oxide*,



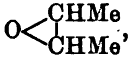
$\begin{matrix}CH_2\cdot CH_2\cdot CMe_2\\ CH_2\cdot CH_2\cdot O\end{matrix}$, which forms a colourless, mobile oil, b. p. 121°, and has an intense odour of camphor. Oxidation of the glycol with potassium permanganate leads to the formation of acetone and succinic acid.

G. Y.

Action of Acetic Anhydride on Di*iso*butylene Glycol. NICOLAUS A. PRILERZAEFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 759—768. Compare Abstr., 1904, i, 795).—The products obtained by the interaction of acetic anhydride and α-glycols depend to a very large extent on the temperature and duration of the experiment. Below 150°, almost the only products produced are diacetyl-α-glycols. At higher temperatures, one acetyl group is split off, forming at least two unsaturated monoacetates, which, on saponification, yield the corresponding alcohols, which in their turn can form a variety of compounds, such as aldehydes, ketones, unsaturated hydrocarbons, &c.

The following compounds are formed when acetic anhydride reacts with di*iso*butylene glycol: (1) a saturated *diacetyl* compound, $C_8H_{16}O_2(COMe)_2$, b. p. 123—125°/12·5 mm., which, on saponification, yielded the *alcohol*, $C_8H_{16}(OH)_2$, b. p. 217—218°/760 mm., m. p. 59—60°; (2) the *monoacetyl* compound of an unsaturated *alcohol*, $C_8H_{15}O(COMe)$, b. p. 190—191°/759·8 mm., D_0^0 0·9067, D_0^{20} 0·8892. On hydrolysis, it yields an *aldehyde* which gives the *silver* salt $C_8H_{15}O_2Ag$, and an unsaturated *alcohol*, $C_8H_{15}\cdot OH$, b. p. 176—178°/762 mm., D_0^0 0·8652, $D_0^{20\cdot5}$ 0·8512, which easily polymerises, forming a substance with a low b. p. and the properties of an aldehyde; (3) these saponification products and their derivatives. The α-glycols themselves are quite stable, but when heated in a sealed tube from which the oxygen has not been exhausted, a small quantity of the glycol is oxidised to a hydroxy-acid, which then acts as a catalyst in converting the glycol into aldehyde, but as the quantity of the catalyst is very slight, a high temperature and prolonged heating are necessary to effect the change. Z. K.

Interaction of Ethyl Bromide and Silver Chromate. ARTHUR JAQUES (*Chem. News*, 1907, **96**, 77).—When silver chromate is treated with ethyl bromide in presence of water, silver bromide is obtained together with a red solution containing alcohol and chromic acid. In the absence of water, a brownish-red solid is produced which is probably *ethyl chromate*, but has not yet been obtained pure. On heating this substance, decomposition occurs with formation of chromic acid, carbon dioxide, water, and other products. Sodium hydroxide decomposes it into alcohol and sodium chromate. E. G.

Symmetrical Dimethylethylene Oxide. LOUIS HENRY (*Compt. rend.*, 1907, **145**, 406—408).—By the action of magnesium methyl bromide on *s*-dimethylethylene oxide,  $O<\begin{matrix}CHMe\\|\\CHMe\end{matrix}$, *αα*-dimethylpropyl alcohol, $CH_2Me\cdot CMe_2\cdot OH$, is formed exclusively. Since the same tertiary alcohol results from the action of magnesium methyl bromide on methyl ethyl ketone (isomeric with dimethylethylene oxide), whilst the oxide as such would be expected to give *αβ*-dimethylpropyl alcohol, $CHMe_2\cdot CHMe\cdot OH$, it is probable that the magnesium compound causes the oxide to undergo isomeric change into the ketone similar to that induced by dilute sulphuric acid in butylene glycol.

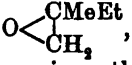
E. H.

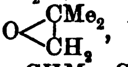
Preparation of the Asymmetrical Halohydrins and Properties of the Corresponding Ethylene Oxides. ERNEST FOURNEAU and MARC TIFFENEAU (*Compt. rend.*, 1907, **145**, 437—439). —By the action of organo-magnesium derivatives on chloroacetone

(Tiffeneau) or ethyl chloroacetate and its homologues (Fourneau), unsymmetrical α-halohydrins are produced together, in some cases, with secondary products of approximately the same boiling point, which are separated from the halohydrins by converting these with alkali into ethylene oxides, or with dimethylamine into aminoalcohols. β-Methyl-α-butylene α-chlorohydrin, $CMeEt(OH)\cdot CH_2Cl$, b. p. 152—153°, D^0 1·068 (compare Abstr., 1902, i, 449), is obtained by the action of magnesium ethyl bromide on chloroacetone.

The secondary product is *β-methyl-α-ethylbutyl alcohol*,

$CHMeEt\cdot CHEt\cdot OH$,

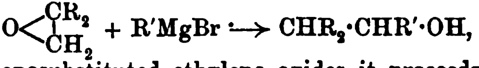
b. p. 149—150° (corr.), D^0 0·8518, which forms a *butyrate*, b. p. 195—198°, D^0 0·883; an *isovalerate*, b. p. 208—209°, D^0 0·837, and a *benzoate*, b. p. 147°/17 mm., D^{16} 0·987, is oxidised into a *ketone*, $C_7H_{14}O$, b. p. 136—138°, D^{19} 0·8248, forming a *semicarbazone*, m. p. 137°, and probably owes its origin to the formation of a *as*-methylethylethylene oxide,  $O<\begin{matrix}CMeEt\\ |\\ CH_2\end{matrix}$, since this forms the same alcohol when treated with magnesium ethyl bromide.

The secondary product in the formation of β-methyl-α-propylene α-chlorohydrin, $CMe_2(OH)\cdot CH_2Cl$, which with alkali gives a *as*-dimethylethylene oxide,  $O<\begin{matrix}CMe_2\\ |\\ CH_2\end{matrix}$, b. p. 51—52°, D^0 0·865, is αβ-dimethylpropyl alcohol, $CHMe_2\cdot CHMe\cdot OH$. Together with β-ethyl-α-butylene α-chlorohydrin, $CH_2Me\cdot CEt(OH)\cdot CH_2Cl$ (compare Dalebroux and Wuyts, this vol., i, 105), which gives an *oxide*, b. p. 105—106°, D^0 0·837, the alcohol $C_8H_{18}O$, b. p. 162—164°, D^0 0·835, which is probably *αβ-diethylbutyl alcohol*,

$CH_2\cdot Me\cdot CHEt\cdot CHEt\cdot OH$,

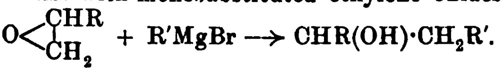
is formed. *αββ-Trimethylethylene α-chlorohydrin*, $OH\cdot CMe_2\cdot CHMeCl$, b. p. 141°, D^0 1·053, *αβ-dimethyl-β-ethylethylene α-chlorohydrin*, $OH\cdot CMeEt\cdot CHMeCl$, b. p. 160—165°, D^0 1·034, and *α-methyl-ββ-diethylethylene α-chlorohydrin*, $OH\cdot CEt_2\cdot CHMeCl$, b. p. 170—174°, D^0 1·021, are prepared by the action of magnesium methyl- or ethyl-bromide on γ-chloro-β-butanone or ethyl-β-chloropropionate. With potassium hydroxide, these give trimethylethylene oxide, dimethylethylethylene oxide, and methyldiethylethylene oxide respectively. The secondary products appear to be tertiary alcohols.

When organo-magnesium compounds act on asymmetrical disubstituted ethylene oxides, the reaction proceeds thus:



$$O<\begin{matrix}CR_2\\ |\\ CH_2\end{matrix} + R'MgBr \longrightarrow CHR_2\cdot CHR'\cdot OH,$$

whilst with monosubstituted ethylene oxides it proceeds as follows:



$$O<\begin{matrix}CHR\\ |\\ CH_2\end{matrix} + R'MgBr \longrightarrow CHR(OH)\cdot CH_2R'.$$

E. H.

Binary Solution Equilibrium between Formic Acid and Water, and between Acetic Acid and Water. **Robert Kremann** [and, in part, **E. Bennesch**, **A. Flooh**, and **F. Kerschbaum**] (*Monatsh.*, 1907, **28**, 893—900).—According to Roscoe (*Annalen*, 1863, **125**, 320), formic acid containing 22·5% of water, corresponding with a hydrate, $4CH_2O_2,3H_2O$, boils constantly at 107°/760 mm. The existence of such a hydrate, as also of Lorin's hydrate, $2CH_2O_2,3H_2O$, appeared improbable since the b. p. of the mixtures vary with the pressure, and as a general rule the composition of hydrates is more simple. To establish this point and to investigate the possible existence of a hydrate, CH_2O_2,H_2O, corresponding with orthoformic acid, the authors determined the freezing points of a series of mixtures of formic acid and water. The freezing point curve falls to one eutectic point at $-53{\cdot}5°$, corresponding with a mixture of 64% of formic acid and 36% of water, hence formic acid does not form a hydrate.

Acetic acid behaves in the same manner; the freezing point curve for mixtures of acetic acid and water falls to one eutectic point at $-27{\cdot}5°$, corresponding with 57·5% of acetic acid and 42·5% of water. The depressions of the freezing points of formic and acetic acids by addition of water, as calculated from their heats of fusion, approximate to the experimental data only when the water is assumed to be bi- or ter-molecular. G. Y.

Rôle of Metallic Hydrides in Reduction. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 607—609. Compare this vol., i, 10).—An excess of cobalt hydride at 270°/760 mm. reduces oleic acid until 28—26% of stearic acid is produced, when the reaction terminates. In sealed tubes the reaction proceeds more readily, 60% of stearic acid being formed. Cobalt, obtained by the reduction of the lower oxide at 310—330°, when heated with a valeric or butyric acid solution of oleic acid at 160—250°, a constant stream of hydrogen being sent through the mixture, produces about 31% of stearic acid in one and a half hours. With reduced nickel, a similar result is obtained at 97—170°, but at the ordinary temperature no reaction takes place in either case. Palladium and platinum black rapidly reduce oleic acid, even at the ordinary temperature. Z. K.

Mercuric Salts of Organic Acids. A. D. DONK (*Rec. trav. chim.*, 1907, **26**, 214—217).—The author has prepared *mercuric glycollate*, $C_4H_6O_6Hg$, and also the *double* salt, $C_4H_6O_6Hg,HgCl_2$ (compare Schreiber, this Journ., 1876, ii, 398). The addition of silver nitrate to an aqueous solution of the double salt produces a white precipitate, which rapidly becomes yellow and dissolves on the addition of nitric acid; but excess of silver nitrate precipitates silver chloride, which does not re-dissolve. Double salts with mercuric chloride are also formed by mercuric acetate, lactate, propionate, and succinate, but apparently not by mercuric diglycollate. In aqueous solution, mercuric acetate is decomposed on heating, with deposition of mercuric oxide, and the *double* salt, $Hg(OAc)_2,HgCl_2$, behaves similarly. The double salt formed by mercuric *propionate*, $(C_3H_5O_2)_2Hg,HgCl_2$, crystallises in mammillary masses of small needles, m. p. about 87°. T. H. P.

Saponification of the Acetates of Glycerol. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1907, **13**, 485—494).—The hydrolysis of the acetates of glycerol is studied in the same way as that of the acetates of glycol (this vol., i, 462), in order to see whether the velocity constants of the reactions: (1) $C_3H_5O_3(COMe)_3 + H_2O = C_3H_6O_3(COMe)_2 + Me{\cdot}CO_2H$; (2) $C_3H_6O_3(COMe)_2 + H_2O = C_3H_7O_3(CO{\cdot}Me) + Me{\cdot}CO_2H$, and (3) $C_3H_7O_3(COMe) + H_2O = C_3H_8O_3 + Me{\cdot}CO_2H$, are in the ratio 3 : 2 : 1. The rate of hydrolysis of the three acetates is determined in 0·01 and 0·02*N* hydrochloric acid at 18° and 25·2°, and the three velocity constants calculated from the results in the same way as before. The velocity constants for normal concentration of the hydrogen ions are :

	18°.	25·2°.
Reaction (1)......................	0·359	0·650
Reaction (2)......................	0·232	0·424
Reaction (3)......................	0·132	0·260

The constants are in the ratio 3·10 : 2·00 : 1·14 at 18°, and 3·06 : 2·00 : 1·25 at 25·2°, that is, in glycerol triacetate the first acetyl group is hydrolysed three times, and the second twice as fast as the third. The experimental results are in good agreement with the view that the hydrolysis takes place in the three stages. T. E.

Glycerides of Fatty Acids. I. Occurrence of Tristearin in Beef and Mutton Tallow. ALOIS BÖMER [and, in part, A. SCHEMM and G. HEIMSOTH] (*Zeitsch. Nahr. Genussm.*, 1907, 14, 90—117).—The author finds that tristearin is present in both beef and mutton tallow, and that under suitable conditions of crystallisation this triglyceride may be obtained from the fats in a perfectly pure state. In this respect, the results of the authors' experiments do not agree with those of Kreis and Hafner, who state that palmityldistearin is present in these fats (Abstr., 1903, i, 457). The beef tallow examined contained 1·5%, and the mutton tallow 3%, of tristearin, whilst a sample of commercial pressed beef tallow contained from 4—5%. A determination of the melting point of glycerides obtained by crystallisation is of considerable use in ascertaining the purity of the specimens; with a pure glyceride, the first and second melting points (Abstr., 1902, i, 529) coincide exactly. W. P. S.

Process of Oxidation of Drying Vegetable Oils. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 609—615. Compare *Zeitsch. angew. Chem.*, 1906, 51, 2087).—Catalytic reactions of oxidation and of reduction are regarded as being of an essentially similar type, and as conforming to Engler's and Weisberg's theories of molecular autoxidation. The activity of the oxygen depends on its molecular state, thus the oxidation of linseed and other oils in the presence of metallic salts proceeds thus: $AO_2 + B \longrightarrow AO + BO$ (where A is a metal and B an oil). Light affects the process of oxidation both in the presence and absence of a catalyst.

The rate of drying of a layer of oil has been found to be in agreement with Spring's rule, being doubled for every 10° rise in temperature. That the reaction of oxidation of the oil is a catalytic one is shown by (1) the absence of any stoichiometric relation between the quantity of metal employed and the amount of oxygen absorbed; (2) the reaction being represented by a logarithmic curve. For the curve representing the first period of the reaction when the absorption of oxygen is proportional to the time, the following equation is proposed: $k = m/t_1 + 1/t_2.lg.a/(a-x)$. The absorption of oxygen seems to be directly proportional to its concentration. When the quantity of the catalyst is diminished, the first period is extended, from which it is deduced that the first phase of the reaction corresponds with molecular autoxidation, and that both molecular and atomic autoxidation can proceed simultaneously.

Old linseed oil, whipped oil, and prepared drying oils dry more quickly than fresh oils because they are already partly oxidised, and for the same reason the former absorb much less oxygen than the latter. The method of preparation of the oil, its freshness, and the material on which the layer is spread all have an important bearing on the mode of the reaction. The following metals act as the strongest catalysts in the process of oxidation: cobalt, manganese, chromium, and nickel, followed by lead, cerium, and barium, the least active being bismuth, mercury, copper, zinc, and uranium. In the process of reduction, the order is reversed. The higher the state of oxidation of the metal employed, the more rapid its effect on the drying up of the layer of oil.

Z. K.

Cotton-seed Oil. Victor J. Meyer (*Chem. Zeit.*, 1907, 31, 793—794).—By applying Haller's process (fractional distillation under reduced pressure of the fatty methyl esters), the author concludes that cotton-seed oil is largely composed of palmitin. L. de K.

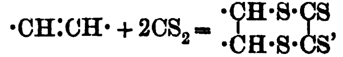
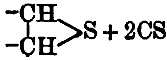
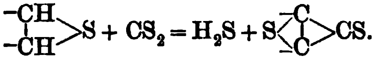
Oil of Myrtle Seeds. Francesco Scurti and F. Perciabosco (*Gazzetta*, 1907, 37, i, 483—486).—The seeds of the myrtle (*Myrtus communis*) contain 12—15% of a fatty oil, which, when extracted with ether or carbon disulphide, is obtained as a yellow liquid dissolving readily in turpentine and sparingly in alcohol. Poutet's elaidin test almost completely decolorises it, but does not convert it into a solid mass. The oil readily solidifies and has the following constants: D^{15} 0·9244; thermal index by Tortelli's thermo-oleometer, 39; acidity, 1·7 c.c. of *N*/10 alkali per gram; saponification number, 199·84; Reichert-Meissl number, 9·65; Hehner's number, 95·31; iodine number, 107·45. It contains glycerides of oleic, linoleic, myristic, and palmitic acids, but not of stearic acid. T. H. P.

Raspberry-seed Oil. Richard Krźiźan (*Zeitsch. offentl Chem.* 1907, 13, 263—267).—A specimen of oil extracted from raspberry seeds gave the following chemical and physical constants: D^{15} 0·9317; saponification number, 192·3; iodine number, 174·8; acid number, 1·0. The seeds yielded about 14·6% of the oil, the unsaponifiable portion of which contained 0·7% of phytosterol. The oil possessed drying properties, but in this respect was inferior to linseed oil. The liquid fatty acids consisted principally of linolic and linolenic acids; small quantities of oleic and *iso*linolenic acids were also present.

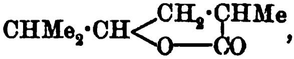
W. P. S.

Reactions of Iodine and of Sulphur with Mercurialised Fatty Substances. Alexandre Leys (*Bull. Soc. Chim.*, 1907, [iv], 1, 633—640. Compare this vol., i, 582).—The iodine number of a fat can be measured in glacial acetic acid solution as well as in alcohol, iodine being decolorised in the former solvent by sodium thiosulphate with formation of sodium iodide and tetrathionate. If mercuric acetate is also present, titration with thiosulphate must be preceded by addition of a moderately large amount of potassium iodide. A certain amount of the iodine is fixed by the mercuric salt, but as this amount is constant, the results are not vitiated. The mercuric acetate solution must not, however, be heated with the fat. In estimating in this way the iodine number of a fat, the latter is dissolved in chloroform and to the solution is added a mixture of mercuric acetate solution and acetic acid solution of iodine, an equal volume of this mixture being titrated, after addition of potassium iodide, with sodium thiosulphate. After two hours, potassium iodide is added and the excess of iodine estimated by titration with thiosulphate. These observations are in contradiction to the views of Wijs (Abstr., 1898, ii, 412). The above method gives for butter and cocoa-butter the numbers 33·6 and 5·1, Hübl's method giving 32·0 and 4·7.

The fact that the amount of iodine which oleic acid or butter is capable of fixing gradually diminishes when the fat is boiled with an acetic acid solution of mercuric acetate is regarded by the author as evidence supporting the view that oxygen is taken up by the fat (see this vol., i, 582).

When cotton-seed oil is heated with carbon disulphide and sulphur in acetic acid, it gives the characteristic coloration of Halphen's reaction. The changes occurring in this reaction are represented by the following equations :  $\cdot CH{:}CH\cdot + 2CS_2 = \begin{matrix}\cdot CH\cdot S\cdot CS\\ | \qquad\qquad |\\ \cdot CH\cdot S\cdot CS\end{matrix}$, which, with S, gives  $\begin{matrix}-CH\\ |\\ -CH\end{matrix}\!>S + 2CS_2$; finally,  $\begin{matrix}-CH\\ |\\ -CH\end{matrix}\!>S + CS_2 = H_2S + S\!<\!\begin{matrix}-C\\ |\\ \geq C\end{matrix}\!>\!CS$.

T. H. P.

Synthesis and Properties of β-Hydroxy-αδ-dimethylheptoic Acid. V. Raichstein (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 587—607).—By the action of ethyl α-bromopropionate on β-methylbutaldehyde in the presence of zinc or zinc-copper, an ester is obtained, b. p. 120—129°/760 mm. The yield of the crude product varies largely with the conditions of the experiment and is better when zinc is employed than with zinc-copper. Owing to decomposition, the ester could not be purified ; it is hydrolysed with difficulty, yielding the free *β-hydroxy-αδ-dimethylhexoic acid*, a colourless, syrupy liquid, with a pleasant odour, soluble in water, ether, and alcohol. On distillation with sulphuric acid, it yields (1) the *lactone*,  $CHMe_2\cdot CH\!<\!\begin{matrix}CH_2\cdot CHMe\\ \qquad\quad |\\ O\text{——}CO\end{matrix}$, b. p. 223—225°, with a camphor-like odour ; (2) an unsaturated *acid*, $CHMe_2\cdot CH_2\cdot CH{:}CMe\cdot CO_2H$, of which the *silver*, *calcium*, and *barium* salts are described. On dry distillation, β-hydroxy-αδ-dimethylheptoic acid yields carbon dioxide, water, aldehydes, and an unsaturated acid.

Its salts with the following metals are soluble in water: *sodium*, *potassium*, *ammonium*, *magnesium*, *calcium*, *barium*, *strontium*, *manganese*, *zinc*, *nickel*, *cobalt*, *silver*, *copper*, and *cadmium*. The following are sparingly soluble: *ferric*, *mercury*, *lead*, *bismuth*, and *tin*. A detailed comparison is given of the properties of β-hydroxy-αδ-dimethylheptoic acid and of its homologues (compare Reformatsky, Abstr., 1897, i, 212). Z. K.

Use of Zinc Chloride in the Esterification of Succinic Acid. ISAAC K. PHELPS and M. A. PHELPS (*Amer. J. Sci.*, 1907, [iv], 24, 194—196).—Almost the full yield of diethyl succinate is obtained by heating a mixture of 50 grams of pure succinic acid and 1 gram of fused zinc chloride with 40 c.c. of alcoholic hydrogen chloride (10 grams to the litre of absolute alcohol) at 100—110°, and then passing a current of gaseous alcohol (160 c.c.). The product is purified by washing with iced water, neutralisation with sodium carbonate, extraction with ether, and subsequent fractional distillation.

L. DE K.

Electrolytic Decomposition of Dicarboxylic Acids. Suberic Acid. B. LINO VANZETTI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 79—84, 139—144. Compare Abstr., 1906, i, 624).—The electrolytic decomposition of a 28·8% aqueous solution of potassium hydrogen suberate between platinum electrodes at about 45°, using a current density of about 0·5 ampere and a voltage of 12, proceeds rapidly and gives rise to a vigorous evolution of carbon dioxide together with a little oxygen and about 1% of carbon monoxide. No hydrocarbons, either saturated or unsaturated, are formed, the principal compounds obtained being unsaturated oxidation products, of which the following have been isolated. A mixture of isomeric unsaturated alcohols, $C_6H_{12}O$; isomeric unsaturated acids, $C_7H_{12}O_2$, and saturated 7-carbon atom acids; the lactone, $C_7H_{12}O_2$, of an acid, the barium salt of which, $(C_7H_{13}O_3)_2Ba$, was prepared; neutral aldehydic compounds; keto- and aldo-acids. T. H. P.

Oxidisability of Aliphatic Aldehydes, especially Formaldehyde. V. CERVELLO and A. PITINI (*Gazzetta*, 1907, 37, i, 577—581).—Animal tissues or extracts of them rapidly attack formaldehyde, which is, however, not transformed into formic acid. This action does not take place if the tissues are treated previously with boiling water. It is found that, when submitted to the action of the tissues in presence of hydrogen peroxide, the aldehyde is oxidised to carbon dioxide, the rate of oxidation varying considerably with the tissues of different organs. No action occurs if either the tissue or the aldehyde is omitted. The same action, which is evidently due to an enzyme, is produced with propaldehyde, valeraldehyde or *iso*butaldehyde. T. H. P.

Action of Barium Peroxide and Hydrogen Peroxide on Formaldehyde. C. ALLAN LYFORD (*J. Amer. Chem. Soc.*, 1907, 29, 1227—1236).—It has been stated by Geisow (Abstr., 1904, i, 289) that when formaldehyde is oxidised with barium peroxide, hydrogen is evolved and barium carbonate is produced. Experiments are now described which show that barium formate and hydrogen are formed together with small quantities of barium hydroxide and hydrogen peroxide. The changes probably take place as follows. A comparatively slow reaction, $CH_2O + BaO_2 + H_2O = H \cdot CO_2H + Ba(OH)_2$, yields formic acid capable of reacting with barium oxide or peroxide. With barium peroxide, it liberates hydrogen peroxide, $2H \cdot CO_2H + BaO_2 = Ba(CO_2H)_2 + H_2O_2$, and the latter reacts with formaldehyde thus: $2CH_2O + H_2O_2 = 2H \cdot CO_2H + H_2$. The last two reactions take place much more rapidly than the first, and when combined give the equation $2CH_2O + BaO_2 = Ba(CO_2H)_2 + H_2$, which represents the change almost quantitatively. The fact that the first reaction takes place to some extent shows that the yield of hydrogen cannot be quantitative.

Geisow (*loc. cit.*) has also stated that the action of hydrogen peroxide on formaldehyde proceeds thus: $CH_2O + H_2O_2 = CO_2 + H_2O + H_2$, and that no free formic acid is produced in any stage of the reaction. It is now found that when hydrogen peroxide reacts with formaldehyde, formic acid is produced as an intermediate product and, on prolonged action, is oxidised to carbon dioxide and water. In one experiment, an estimation of the formic acid produced gave a result equivalent to 79·36% of the formaldehyde taken. The reaction is expressed approximately by the equations $2CH_2O + H_2O_2 = 2H \cdot CO_2H + H_2$ and $2H \cdot CO_2H + 2H_2O_2 = 2CO_2 + 4H_2O$. E. G.

Preparation of Propaldehyde. MARIO MARCHIONNESCHI (*Gazzetta*, 1907, **37**, ii, 201—204).—To increase the yield of propaldehyde, prepared by the action of chromic acid mixture on propyl alcohol, the author inserts a reflux condenser kept at 30° between the flask in which the reagents are heated and the ordinary condenser. In this way, the yield of aldehyde is approximately quadrupled. If pure propyl alcohol is employed instead of the ordinary alcohol, the process of separating the aldehyde by fractionation is greatly facilitated.

T. H. P.

Condensation Products of Glyoxal and *iso*Butaldehyde. HUGO ROSINGER (*Monatsh.*, 1907, **28**, 947—960).—The condensation of glyoxal and *iso*butaldehyde has been re-studied as definite results were not obtained by Hornbostel and Siebner (Abstr., 1900, i, 206). When boiled together in alcoholic potassium hydroxide solution, glyoxal and *iso*butaldehyde yield only *iso*butyric acid and Fossek's octylene glycol, but on condensation in aqueous solution in presence of potassium carbonate at the ordinary temperature form a crystalline substance, $C_{10}H_{18}O_4$, a *liquid*, $C_{10}H_{20}O_3$, *iso*butaldol, and *acetiso*butaldol.

The substance $C_{10}H_{18}O_4$ was isolated by Hornbostel and Siebner; it separates from water in rhombohedra, m. p. 130°, or from ether in crystals, m. p. 55°, b. p. 140°/14 mm., sublimes in needles, reduces ammoniacal silver solutions in the cold, and is considered to have the constitution $CHO \cdot CMe_2 \cdot CH(OH) \cdot CH(OH) \cdot CMe_2 \cdot CHO$. On reduction with aluminium amalgam and alcohol, it yields the tetrahydroxy-compound, $OH\cdot CH_2\cdot CMe_2\cdot CH(OH)\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH$, which forms transparent crystals, m. p. 127°.

The *liquid*, $C_{10}H_{20}O_3$, b. p. 114°/14 mm., is considered to have the constitution $OH\cdot CHMe\cdot CMe_2\cdot CH(OH)\cdot CMe_2\cdot CHO$; when distilled under atmospheric pressure, it yields *iso*butaldehyde, and on distillation with dilute sulphuric acid yields a strongly reducing distillate, which has an odour of crotonaldehyde and contains *iso*butaldehyde. It is reduced by aluminium amalgam, forming the *product*,

$$OH\cdot CHMe\cdot CMe_2\cdot CH(OH)\cdot CMe_2\cdot CH_2\cdot OH,$$

which is obtained as a slightly green liquid, b. p. 132°/16 mm.

The formation of the liquid product, $C_{10}H_{20}O_3$, and of acet*iso*butaldehyde is ascribed to the presence of metaldehyde in the glyoxal prepared by Hornbostel and Siebner's method; in agreement with this view, the glyoxal, when heated at 150° under pressure, has an odour of acetaldehyde, and when distilled into an ethereal solution of ammonia forms aldehydeammonia. G. Y.

Isomerism of Aldoximes. KARL BECK and P. HASE (*Annalen*, 1907, **355**, 29—57).—A comparative study of the α- and β-oximes of benzaldehyde, anisaldehyde, cuminaldehyde, and *m*-nitrobenzaldehyde.

Alcoholic solutions of the β-oximes, but not of the α-oximes, give intense blood-red colorations with ferric chloride and yellowish-green to olive-green colorations with copper acetate.

The β-oximes of benzaldehyde, anisaldehyde, and cuminaldehyde give at once with silver nitrate in alcoholic solution white, crystalline precipitates. These *additive* compounds decompose at 98—125°, and have the composition 2 mols. oxime + 1 mol. silver nitrate.

These oximes also give crystalline precipitates with mercurous nitrate in alcoholic solution; the *additive* compounds so obtained are not pure; they probably have the composition 1 mol. oxime + 1 mol. mercurous nitrate. The α-oximes do not give precipitates with mercurous and silver nitrates. It is therefore highly probable that of the two isomeric oximes described by Ratz (Abstr., 1906, i, 238), the one (so-called α-oxime) which forms an additive compound with silver nitrate really has the β-configuration, and vice versa.

Both α- and β-oximes combine with chloral and bromal, forming totally different *additive* compounds; all have, however, the general formula: 1 mol. oxime + 1 mol. bromal or chloral. The α-oxime compounds crystallise in colourless needles, the β-derivatives in large, colourless crystals.

The *α-benzaldoxime* and *α-anisaldoxime chloral* additive compounds melt at 57° and 71° respectively; a compound with α-cuminaldoxime could not be obtained. The *bromal* additive compounds of *α-benzaldoxime*, *α-anisaldoxime*, and *α-cuminaldoxime* melt respectively at 64°, 78°, and 75°.

The *chloral* additive compounds of *β-benzaldoxime*, *β-anisaldoxime*, and *β-cuminaldoxime* melt respectively at 78°, 90°, and 77°, whilst the corresponding *bromal* derivatives melt at 95°, 99°, and 85°.

Except in the case of the β-cuminaldoxime choral compound, which dissociates into the free α-oxime and chloral, the β-compounds change into the α-compounds when kept and in the presence of traces of acid. The β-compounds behave like the β-oximes towards ferric chloride and copper acetate, whilst with silver and mercurous nitrates they give the same compounds as are obtained from the free β-oximes.

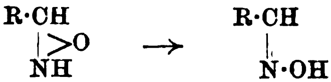
The α-additive compounds do not show any reaction with these four reagents. The α-oxime chloral compounds may also be prepared by the action of chloralhydroxylamine on the aldehydes. It is remarkable that by this method it is possible to obtain the *α-cuminaldoxime chloral* additive compound, m. p. 63°.

The isomeric *m*-nitrobenzaldoximes and the *N*-benzyl ethers of benzaldoxime and anisaldoxime do not combine with chloral or bromal.

Corresponding with the two isomeric carbanilido-β-benzaldoximes obtained by Beckmann (Abstr., 1891, 193), the authors have obtained a second, very labile *carbanilido-β-cuminaldoxime*, $C_{17}H_{14}O_2N_2$, as a yellow, amorphous powder by adding phenylcarbimide to a solution of the β-oxime in light petroleum; after a time, more quickly on warming, it changes into the white form, m. p. 104° (Goldschmidt, Abstr., 1890, 251). These isomeric carbanilido-β-aldoximes behave differently towards ferric chloride and copper acetate. The yellow carbanilido-derivatives of β-benzaldoxime, m. p. 74°; β-anisaldoxime, m. p. 80°; β-cuminaldoxime and β-*m*-nitrobenzaldoxime, m. p. 77° (compare Beckmann, Abstr., 1891, 193, and Goldschmidt and Reitschoten, Abstr., 1893, i, 707), give with ferric chloride in alcoholic solution, at first a red, then a dirty green, and finally an intense blue, coloration, which disappears on long-continued boiling. With copper acetate, is obtained at first a yellowish-green coloration which quickly becomes dirty green, followed by the appearance of a greyish-green, flocculent precipitate. If, however, the alcoholic solution of the substance is heated, or the substance itself is warmed before dissolution, and ferric chloride then added, only a faint red or yellow coloration is obtained. This same faint coloration is obtained by adding ferric chloride to the alcoholic solution of the white carbanilido-derivatives of β-benzaldoxime, m. p. 94°, and β-cuminaldoxime, m. p. 104°; these compounds give a yellowish-green coloration with copper acetate, but not a precipitate. The carbanilido-α-oximes do not react with ferric chloride or copper acetate.

The carbanilido-derivatives obtained synthetically by the action of *s*-phenylhydroxycarbamide on the aldehydes in ethereal solution are identical with the carbanilido-α-oximes prepared by the action of phenylcarbimide on the α-oximes (Goldschmidt and Rietschoten, *loc. cit.*).

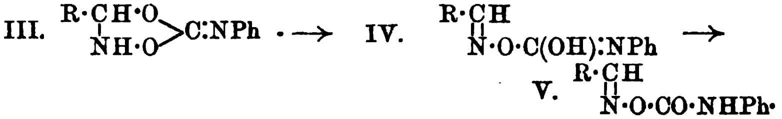
The authors consider that the β-oximes (I) have a different structure from the α-oximes, the power of reacting in the tautomeric, α-oxime stereoisomeric, form (II) depending on the ready wandering of the *N*-hydrogen atom:



$$\text{I.}\quad \begin{array}{c}\text{R·CH}\\ |\!>\!\text{O}\\ \text{NH}\end{array} \quad\longrightarrow\quad \begin{array}{c}\text{R·CH}\\ \|\\ \text{N·OH}\end{array}\quad \text{II.}$$

The yellow carbanilido-derivatives probably have the formula (III) and pass into the colourless form (V) through the intermediate form

(IV); the colorations which the yellow compounds give with ferric chloride are probably due to the formation of this enolic form:



$$\text{III.}\ \begin{matrix}R\cdot CH\cdot O\\ |\\ NH\cdot O\end{matrix}\!\!>\!C{:}NPh \longrightarrow \text{IV.}\ \begin{matrix}R\cdot CH\\ \|\\ N\cdot O\cdot C(OH){:}NPh\end{matrix} \longrightarrow \text{V.}\ \begin{matrix}R\cdot CH\\ \|\\ N\cdot O\cdot CO\cdot NHPh\end{matrix}$$

The colourless form would then readily change into the *a*-(*anti*-) derivative. It is further argued that since chloralhydroxylamine and phenylhydroxycarbamide combine with aldehydes yielding *a*-oxime derivatives, they have the formulæ $CCl_3\cdot CH(OH)\cdot O\cdot NH_2$ and $NHPh\cdot CO\cdot O\cdot NH_2$. W. H. G.

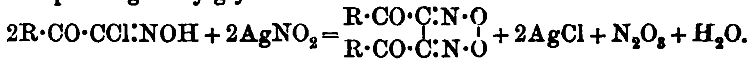
Catalytic Reactions at High Temperatures and Pressures. XIII. Reducing Catalysts. WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 681—692. Compare this vol., i, 5, 6, 457). —The apparatus formerly used for high pressure experiments has been further improved. Acetone when heated in an iron tube in the absence of hydrogen only commences to change at about 420°, when an oil insoluble in and lighter than water is formed, together with a small quantity of carbon dioxide and methane. In the presence of hydrogen at 400°, acetone is reduced to *iso*propyl alcohol, but equilibrium is established when 25% of the acetone has suffered change; a small quantity of the above oil is also formed. *iso*Butaldehyde does not react with hydrogen in the absence of iron. In the presence of iron, but absence of hydrogen, the aldehyde at 400° yields condensation products, carbon monoxide, and small quantities of carbon dioxide and hydrogen. *iso*Butyl alcohol, under the same conditions, yields the same gases, much hydrogen, and *iso*butaldehyde. In an iron tube and in the presence of hydrogen, *iso*butaldehyde is almost wholly converted into the alcohol. *iso*Valeraldehyde behaves similarly, one of the products being amylene. Both ordinary and reduced iron can act as reducing catalysts in all those cases in which reduced nickel can be employed, but the necessary temperature for the latter is much lower. *iso*Propyl alcohol in the presence of reduced nickel at 200—230° reacts thus: $CHMe_2\cdot OH\cdot Me \rightleftharpoons H_2+COMe_2$, the products of the reaction being acetone, *iso*propyl alcohol, hydrogen, and methane. Complete equilibrium is reached only after very prolonged heating. In the presence of an excess of hydrogen, acetone is wholly converted into the alcohol at temperatures not exceeding 210—220°. Above this, the reaction is reversible. Methyl ethyl ketone and the carbinol and *iso*amyl alcohol behave similarly to the *iso*propyl derivatives, under the same conditions, only the corresponding temperatures are higher. Methyl alcohol yields methane, hydrogen, carbon dioxide, and water. Benzene in the presence of iron, without hydrogen, yields hydrogen and diphenyl above 600°. In the presence of hydrogen, the reaction also only commences above 500°, but employing reduced nickel and hydrogen, pure *cyclo*hexane is formed at 255°, but above 300° benzene, methane, and carbon are also formed. Z. K.

Catalytic Reactions at High Temperatures and Pressures. XIV. Reducing Catalysts in the Presence of Metallic Oxides.

WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 693—702. Compare preceding abstract).—The oxides of nickel have been found to bring about the catalytic reduction of benzene, acetone, *iso*propyl alcohol, diphenyl, naphthalene, dibenzyl, α- and β-naphthols, and benzophenone much more quickly than reduced nickel, the pure saturated reduction products being obtained in each case. Nickelic oxide is a better catalyst than nickelous oxide. The reaction proceeds much faster if the oxide is placed at the surface of the liquid than if the latter is poured on to it. The rate of the reaction is considerably diminished by decreasing the amount of catalyst. Time-temperature curves and tables are given. Z. K.

Action of Silver Nitrite on Chloro*iso*nitrosoketones.

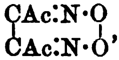
GIACOMO PONZIO and G. CHARRIER (*Gazzetta*, 1907, **37**, ii, 65—71).—Chloro*iso*nitrosoketones, when treated with silver nitrite, are not converted into nitrolic acids, as might be expected (compare Piloty and Steinbock, Abstr., 1902, i, 735), but into peroxides of the corresponding diacylglyoximes:



$$2\mathrm{R\cdot CO\cdot CCl\!:\!NOH} + 2\mathrm{AgNO_2} = \begin{array}{l}\mathrm{R\cdot CO\cdot C\!:\!N\cdot O}\\ \mathrm{R\cdot CO\cdot C\!:\!N\cdot O}\end{array} + 2\mathrm{AgCl} + \mathrm{N_2O_3} + \mathrm{H_2O}.$$

Improved methods are given for the preparation of certain chloro*iso*nitrosoketones (compare Claisen and Manasse, Abstr., 1893, i, 464).

The interaction of chloro*iso*nitrosoacetophenone and silver nitrite yields dibenzoylglyoxime peroxide, which has been prepared by Holleman (Abstr., 1888, 275; 1889, 49) by the action of nitric acid on acetophenone or *iso*nitrosoacetophenone and by Angeli (Abstr., 1893, i, 355) by the action of nitric acid on dibenzoylglyoxime.



Diacetylglyoxime peroxide, $\begin{array}{l}\mathrm{CAc\!:\!N\cdot O}\\ \mathrm{CAc\!:\!N\cdot O}\end{array}$, prepared from chloro*iso*nitrosoacetone and silver nitrite, was obtained as a faintly yellow, unstable oil, which could not be purified.

The following new derivatives of chloro*iso*nitrosoacetone have been prepared.

*Chloro*iso*nitrosoacetone phenylhydrazone*, $\mathrm{NHPh\cdot N\!:\!CMe\cdot CCl\!:\!NOH}$, crystallises from chloroform in yellowish-brown, shining needles, m. p. 124° (decomp.), and dissolves readily in alcohol or ether, and to a less extent in benzene. The *semicarbazone*,

$$\mathrm{NH_2\cdot CO\cdot NH\cdot N\!:\!CMe\cdot CCl\!:\!NOH},$$

separates in white prisms, m. p. 158° (decomp.), and dissolves in alcohol or water, the latter decomposing it on heating.

*Acetylphenyl*iso*urethine*, $\mathrm{NOH\!:\!CAc\cdot NHPh}$, prepared by the interaction of aniline and chloro*iso*nitrosoacetone in ethereal solution, crystallises from alcohol in faintly yellow plates, m. p. 119°, and dissolves readily in benzene or chloroform and sparingly in ether.

Acetyl-p-*tolyl*iso*urethine*, $\mathrm{NOH\!:\!CAc\cdot NH\cdot C_6H_4Me}$, crystallises from alcohol in white laminæ, m. p. 130°, and dissolves readily in benzene or chloroform and sparingly in ether. T. H. P.

Derivatives of *iso*Nitrosoketones. G. Charrier (*Gazzetta*, 1907, **37**, ii, 145—148).—The best method, giving a yield of 75—80%, of preparing *iso*nitrosoacetone is from ethyl acetoacetate and sodium nitrite. When crystallised from a mixture of ether and light petroleum, it has m. p. 69°; Meyer and Zublin (Abstr., 1878, 659) gave 65°.

The *oxime* of the *methyl ether* of *iso*nitrosoacetone,

$$NOH\!:\!CMe\cdot CH\!:\!NOMe,$$

crystallises from light petroleum in long, shining needles, m. p. 73°. The corresponding *phenylhydrazone*, $N_2HPh\!:\!CMe\cdot CH\!:\!NOMe$, crystallises from aqueous alcohol in yellow needles, m. p. 104°. The *semicarbazone*, $CONH_2\cdot N_2H\!:\!CMe\cdot CH\!:\!NOMe$, crystallises from water in plates, m. p. 212—213°, and dissolves in alcohol.

The *oxime* of the *methyl ether* of *iso*nitrosomethylethylketone, $NOH\!:\!CMe\cdot CMe\!:\!NOMe$, crystallises from light petroleum in needles, m. p. 104°. The *phenylhydrazone*, $N_2HPh\!:\!CMe\cdot CMe\!:\!NOMe$, crystallises from alcohol in yellow prisms, m. p. 56°. The *semicarbazone*,

$$NH_2\cdot CO\cdot N_2H\!:\!CMe\cdot CMe\!:\!NOMe,$$

crystallises from water or alcohol in white prisms, m. p. 237° (decomp.). T. H. P.

***N*-Alkylketoximes.** Ernst Beckmann and Johannes Scheiber (*Annalen*, 1907, **355**, 235—247).—Acetone reacts with certain β-substituted hydroxylamines to form substances which are presumably *N*-substituted ketoximes. Phenylhydroxylamine yields a *substance*, $C_{18}H_{22}O_2N_2$, m. p. 136° (decomp.); *p*-tolylhydroxylamine yields a mixture of azoxytoluene and a *substance*, $C_{20}H_{26}O_2N_2$, m. p. 157°; *m*-tolylhydroxylamine forms the *substance*, $C_{20}H_{26}O_2N_2$, m. p. 144·5° (decomp.); naphthylhydroxylamine yields azoxynaphthalene and a *substance*, $C_{26}H_{26}O_2N_2$, m. p. 138° (decomp.). This behaviour of acetone is not exhibited by its homologues, acetophenone, or aromatic ketones. Ethyl acetoacetate, however, condenses with phenylhydroxylamine and with *p*-tolylhydroxylamine, yielding substances having m. p. 120·5° and 172° respectively. These will be described subsequently.

The paper contains a résumé of investigations on the alkylation of oximes. C. S.

The Lævorotation of Mannose. William Alberda van Ekenstein and Jan J. Blanksma (*Chem. Weekblad*, 1907, **4**, 511—514).—Lævorotatory mannose in solution is partially transformed into another (mutarotatory) modification the dextrorotation of which largely exceeds +14·2° (+20·9°; +23·5°), the reaction being unimolecular. The velocity of transformation is greater in aqueous solution than in aqueous alcoholic solution. On treatment with methyl sulphate and potassium carbonate, mannose yields α-methylmannoside.

A. J. W.

Action of Ammonium Persulphate Solution on Cellulose. I. Formation and Properties of Cellulose Peroxide. Hugo Ditz (*Chem. Zeit.*, 1907, **31**, 833—834, 844—845, 857—858. Compare Cross and Bevan, *Zeitsch. angew. Chem.*, 1907, **20**, 570).—When heated gently with ammonium persulphate solution acidified with sulphuric acid, filter paper and sulphite cellulose form a peroxide which, after being washed with cold water until free from persulphate, liberates iodine from potassium iodide, but is decomposed by hot water or when dried at 100°. The oxidised cellulose contains about 0·015% of active oxygen; the peroxide formation takes place to a smaller extent with potassium persulphate and to only a slight extent in the absence of free sulphuric acid. The peroxide contains an organic acid which is insoluble or only sparingly soluble in water, since after being washed with water it gives an acid reaction with methyl-orange on addition of an aqueous solution of a neutral alkali salt. Stearic acid behaves towards methyl-orange in the same manner (compare Syzszkowski, this vol., ii, 238). The active oxygen is not concerned in this acid reaction, as after addition of potassium chloride and neutralisation with an alkali, the product still liberates iodine from potassium iodide.

Cellulose, which has been oxidised with ammonium persulphate, reduces Fehling's solution when heated, and with dilute potassium hydroxide gives a yellow coloration becoming golden-yellow when heated; hence it contains oxycellulose (Nastukoff, Abstr., 1900, i, 540). The acid present in the oxidised cellulose may be Buncke and Wolffenstein's acid cellulose (Abstr., 1899, i, 852). Whilst filter paper, on treatment with ammonium persulphate in absence of sulphuric acid, forms oxycellulose, the acid product, and traces of the peroxide, the product obtained on heating filter paper with dilute sulphuric acid only at 70°, contains hydrocellulose and traces of an acid, but not oxycellulose or the peroxide. Similar results are obtained with cotton wool, but the peroxide formation takes place to a smaller extent than with filter-paper, sulphite-cellulose, or linen.

Comparative experiments with filter paper, 20% ammonium persulphate solution, and sulphuric acid (1 : 4) were performed at 20—25°, 40°, and 65°. Evolution of gas took place only slowly at the lowest temperature, more quickly at 40°, and violently at 65°; only in the last case had the gas the characteristic irritating odour of "active" oxygen. In the first two experiments, the filter paper retained its form, but at the highest temperature it was swollen and partially disintegrated. The amounts of the peroxide and of the acid formed increase with the rise in temperature of the reaction, whilst that of the oxycellulose is slightly greater at 40° than at 20—25°, but increases only very slightly when the temperature of the reaction is raised to 65°.

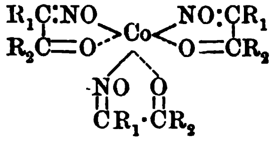
Cellulose peroxide, when moist, decomposes completely in two to three days, but if washed with alcohol and ether remains unchanged for eighteen days, and after thirty-three days still gives a violet coloration with potassium iodide-starch solution. G. Y.

Ring Formation of Complex Compounds. LEO TSCHUGAEFF [and, in part, KARASSEFF] (*J. pr. Chem.*, 1907, [ii], 76, 88—93).—Further evidence is cited in support of the author's views (this vol., i., 17, 392). The stable, bluish-violet *trimethylenediamine nickel sulphate*, $Ni(Tr)_2SO_4$ (Tr = trimethylenediamine), corresponding with the thiocyanate, $Ni(Tr)_2(SCN)_2$ (Abstr., 1906, i, 814), has been prepared.

Excess of trimethylenediamine leads to the formation of a very unstable sulphate of the triamine series. However, a stable *platinosochloride*, $Ni(Tr)_3PtCl_4$, is readily prepared by adding potassium platinochloride to the solution obtained by the addition of an excess of trimethylenediamine to an aqueous solution of nickel chloride.

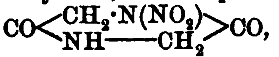
Nickel salts also react with the two stereoisomeric modifications of βδ-diaminopentane, yielding stereoisomeric complex compounds, in the proportion of 1 atom of nickel to 2 mols. of the amine. These compounds are under investigation.

It is found that *a*-oximinoketones behave, in general, like nitroso-β-naphthol (Ilinsky and Knorre, Abstr., 1885, 840) in yielding very stable cobalt derivatives. Thus, the brownish-red, crystalline *compound*, $(COPh{\cdot}CPh{\cdot}NO)_3Co$, is formed by adding a cobalt salt to a solution of *a*-benzilmonoxime in dilute alcohol, in the presence of an excess of ammonium acetate. Analogous iron, nickel, and palladium compounds have also been obtained; they are distinguished by their relatively great stability, abnormal colour, and absence of the ionic reactions of the metals.



The above general formula is proposed for these compounds.

W. H. G.

Nitration of Glycine Anhydride. A. D. Donk (*Rec. trav. chim.*, 1907, **26**, 207—213).—When dissolved in concentrated nitric acid, glycine anhydride yields a product, m. p. about 235° (decomp.), which the analytical numbers indicate to be a dinitrate of the anhydride, whilst titration with potassium hydroxide gives values in agreement with those for a mononitrate. When treated with acetic anhydride, this compound is transformed into *nitroglycine anhydride*,  $CO{<}\begin{matrix}CH_2{\cdot}N(NO_2)\\NH\text{——}CH_2\end{matrix}{>}CO$, which crystallises from methyl alcohol in shining, colourless needles or prisms, m. p. 165° (decomp.), and dissolves sparingly in ether, ethyl acetate, acetone, or alcohol; treatment with methyl-alcoholic potassium hydroxide yields *nitroaminoacetylaminoacetic acid*, $NO_2{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, m. p. 153° (decomp.). An attempt to prepare this acid by the action of nitric acid on ethyl carbethoxyglycylglycine,

$$CO_2Et{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et,$$

resulted in the formation of a nitro-derivative (?) of the latter.

T. H. P.

Monoamino-Acids from Avenine. Emil Abderhalden and Yuho Hämäläinen (*Zeitsch. physiol. Chem.*, 1907, **52**, 515—520).—When hydrolysed with boiling concentrated hydrochloric acid, avenine gives the following amounts of amino-acids, calculated on 100 parts of avenine dried at 100° free from ash: glycine 1·0, alanine 2·5, valine 1·8, leucine 15·0, proline 5·4, aspartic acid 4·0, glutamic acid 18·4, phenylalanine 3·2, and tyrosine 1·5. The results differ from those obtained for legumin mainly in the amounts of tyrosine and leucine (Abderhalden and Babkin, Abstr., 1906, i, 546).

J. J. S.

Certain Derivatives of *s*-Diaminoacetone (1 : 3-Diaminopropanone). ANTOINE P. N. FRANCHIMONT and HERMANN FRIEDMANN (*Rec. trav. chim.*, 1907, **26**, 223—227).—*Methyl acetone-αγ-diaminoacetate*, $CO(CH_2\cdot NH\cdot CO_2Me)_2$, prepared by the action of methyl chloroformate (1—2 mols.) on 1 : 3-diaminopropanone hydrochloride (1 mol.) in presence of sodium hydroxide, carbonate, or acetate, crystallises from alcohol in needles, m. p. 154°.

The *αγ-dinitro*-compound, $CO[CH_2\cdot N(NO_2)\cdot CO_2Me]_2$, prepared by the action of concentrated nitric acid on the preceding compound, crystallises from ether in stellar aggregates of slender needles, m. p. 77°, and dissolves readily in alcohol.

1 : 3-*Diacetylaminoacetone*, $CO(CH_2\cdot NHAc)_2$, prepared by acetylating diaminoacetone, crystallises from alcohol in nacreous spangles, m. p. 200°, and dissolves readily in water and sparingly in ether.

T. H. P.

Preparation of Formamide from Ethyl Formate and Ammonium Hydroxide. ISAAC K. PHELPS and C. D. DEMING (*Amer. J. Sci.*, 1907, [iv], **24**, 173—175).—Hofmann (Abstr., 1882, 950) has stated that when ethyl formate is left with aqueous ammonia at the ordinary temperature, a large proportion of the formamide produced is converted into ammonium formate, and that for this reason the maximum yield of amide obtainable is not much more than 70%.

It is now found that a theoretical yield of formamide can be obtained by treating ethyl formate, cooled below 0°, with a small quantity of cold aqueous ammonia of D 0·90, and passing dry ammonia into the mixture; or more easily by adding a large quantity of solution of ammonia to the ester, both cooled below 0°. In each case, the mixture is left for about five hours, and then distilled in a vacuum. By keeping the temperature low, the production of ammonium formate is avoided.

E. G.

Molecular Magnitude of Oxamide. CONCETTO MASELLI (*Gazzetta*, 1907, **37**, ii, 135—136).—The properties of oxamide, especially its insolubility and high melting point, when compared with those of the corresponding amides of other dibasic acids, would indicate that its molecule is polymerised. Using Bleier and Kohn's apparatus (Abstr., 1899, ii, 643; 1900, ii, 192) heated externally with acetanilide vapour, the author finds that the molecular weight of oxamide at about 300° and under a pressure of a few mm. is 141·21—143·63 instead of 88.

T. H. P.

New Oxalhydroxamic Acid. VINCENZO PAOLINI (*Gazzetta*, 1907, **37**, ii, 87—91).—The author has prepared the third oxalhydroxamic acid, isomeric with the two already known (compare Lossen, *Annalen*, 1869, **150**, 314; Hantzsch and Urban, Abstr., 1895, i, 393).

Oxalhydroxamic acid, $NOH:C(OH)\cdot C(OH):NOH$, prepared by the action of benzenesulphohydroxamic acid on glyoxal in presence of potassium hydroxide (compare Rimini, Abstr., 1901, i, 450), crystallises from a mixture of alcohol and ether in shining, white, hygroscopic laminæ, m. p. 82—83°, dissolves readily in water giving an acid solution, gives an intense cherry-red coloration with ferric chloride, and yields oxalic acid and hydroxylamine when heated with sulphuric acid. Its *copper* salt, $C_2O_4N_2Cu_2$, was analysed. T. H. P.

Reaction between Barium Thiocyanate and Bromoacetic Acid dissolved in Acetone. HENRI DEMIERRE and MARCEL DUBOUX (*J. Chim. Phys.*, 1907, **5**, 340—343. Compare this vol., ii, 75).—The progress of the reaction in question, represented by the equation $Ba(CNS)_2 + 2CH_2Br{\cdot}CO_2H = BaBr_2 + 2CNS{\cdot}CH_2{\cdot}CO_2H$, has been followed by estimating the barium in solution at definite intervals by means of sulphuric acid; the applicability of this method depends on the fact that whilst barium thiocyanate is soluble in acetone, the bromide is insoluble in this medium and can be filtered off. The rate of the reaction is proportional to the concentrations of the thiocyanate and bromoacetic acid respectively, but the constants calculated for a bimolecular reaction diminish somewhat as the initial concentration is increased, and it is therefore suggested that the reaction is ionic. The mean temperature coefficient for 10° between 29·7° and 41·8° is 2·52. G. S.

Interpretation of the Reaction between Ferric Chloride and Potassium Thiocyanate. C. BONGIOVANNI (*Gazzetta*, 1907, **37**, i, 472—475).—The author shows that no ferrous salt is formed in the interaction of freshly precipitated ferric hydroxide and potassium thiocyanate in an atmosphere of nitrogen. It is also found that a solution containing ferric chloride and potassium oxalate undergoes a continual diminution in acidity, seemingly owing to the formation of complex ions, whilst if potassium thiocyanate is also present, no such diminution in the acidity occurs (compare Tarugi, Abstr., 1905, i, 176). The interpretation of the reaction between ferric chloride and potassium thiocyanate given by Magnanini (Abstr., 1891, 1150), namely, $FeCl_3 + 3KCNS \rightleftarrows 3KCl + Fe(CNS)_3$, best explains the observations. T. H. P.

Action of Cyanogen Bromide on Hydrazine. II. GUIDO PELLIZZARI and F. RONCAGLIOLO (*Gazzetta*, 1907, **37**, i, 434—446).—The compound, m. p. about 230°, obtained together with diaminoguanidine and guanazine by the interaction of cyanogen haloid and hydrazine in aqueous solution (Pellizzari and Cantoni, Abstr., 1905, i, 576), is shown to be aminocarbocarbazide or hydrazodicarbonamide, $NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, which has also been synthesised from carbazide and potassium cyanate. The formation of this compound in the above reaction is probably due to part of the diaminoguanidine formed undergoing transformation in the alkaline liquid to carbazide, whilst some of the cyanogen chloride and potassium hydroxide interact to yield potassium cyanate. If carbazide dihydrochloride is treated with potassium cyanate, the main product is diaminodicarbocarbazide, $CO(NH{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, which can also be obtained by the action of potassium cyanate on aminocarbocarbazide. Certain of the transformation products of the latter compound have also been studied.

Aminocarbocarbazide, $NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, best obtained by the gradual addition of acetic acid to a cold solution containing carbazide (1 mol.) and potassium cyanate (1 mol.) until the liquid becomes acid, separates from water in minute, white crystals, m. p. 228° (decomp.), and is insoluble in organic solvents, but dissolves in mineral acids, from which it is precipitated by addition of ammonia. It reduces energetically Fehling's solution and ammoniacal silver nitrate solution. Aldehydes and ketones react with it in acid aqueous solutions. When heated at 226°, it is converted into ammonia and urazine (dicarbamide).

Benzylideneaminocarbocarbazide,

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot N:CHPh,$$

forms a white powder, m. p. 212°.

Salicylideneaminocarbocarbazide, $C_2H_5O_2N_5:CH\cdot C_6H_4\cdot OH$, forms a yellow, crystalline precipitate, m. p. 218°.

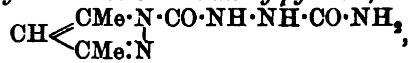
Phenylethylideneaminocarbocarbazide, $C_2H_5O_2N_5:CMePh$, from acetophenone, forms a white, crystalline precipitate, m. p. 214°.

Phenylbenzylideneaminocarbocarbazide, $C_2H_5O_2N_5:CPh_2$, from benzophenone, crystallises from alcohol in shining, white needles, m. p. 222°.

Benzoylbenzylideneaminocarbocarbazide, $C_2H_5O_2N_5:CPhBz$, from benzil, forms a white, crystalline precipitate, m. p. 240°.

Diaminodicarbocarbazide, $CO(NH\cdot NH\cdot CO\cdot NH_2)_2$, is deposited from water in minute, white crystals, m. p. 232° (decomp.), and does not react with benzaldehyde or dissolve in dilute acids.

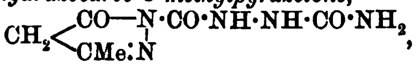
1-*Aminocarbohydrazocarbo*-3 : 5-*dimethylpyrazole*,



$$CH{<}\begin{matrix}CMe\cdot N\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2\\ CMe:N\end{matrix},$$

prepared by the interaction of acetylacetone (1 mol.) and aminocarbocarbazide (1 mol.) in acidified aqueous solution, separates from alcohol in minute, white crystals, m. p. 166°, and is sparingly soluble in water.

1-*Aminocarbohydrazocarbo*-3-*methylpyrazolone*,



$$CH_2{<}\begin{matrix}CO{-}N\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2\\ CMe:N\end{matrix},$$

prepared by the action of ethyl acetoacetate on aminocarbocarbazide, forms white crystals, m. p. 186°.

Aminocarbocarbazide also yields crystalline products with alloxan, citral, and chloral.

The action of cyanogen bromide on hydrazine sulphate yields hydrazodicarbonamide and guanazine hydrobromide. T. H. P.

Constitution of Organo-magnesium Derivatives. EDMOND É. BLAISE (*Bull. Soc. chim.*, 1907, [iv], 1, 610—612).—Evidence is quoted in support of Baeyer and Villiger's formula for organo-magnesium compounds, $R\cdot Mg\cdot OX:Et_2$. T. H. P.

Laws of Substitution in Aromatic Compounds. III. BERNHARD FLÜRSCHEIM (*J. pr. Chem.*, 1907, [ii], 76, 165—179. Compare Abstr., 1903, i, 79; 1905, i, 614; 1906, ii, 529).—A reply to

Holleman (Abstr., 1906, i, 818) and a criticism of Obermiller's views (this vol., i, 200). G. Y.

Laws of Substitution in Aromatic Compounds. IV. BERNARD FLÜRSCHEIM (*J. pr. Chem.*, 1907, [ii], 76, 185—204. Compare Abstr., 1903, i, 79; 1905, i, 614; 1906, ii, 527, and preceding abstract).—The argument of this theoretical paper is based on the following conceptions of the mode of action of chemical affinity.

(1) Part of the affinity of all atoms remains free when these form chemical compounds, the free affinity being in equilibrium with the combined. The reactivity of the molecule, so far as not determined by electrolytic dissociation, depends on this free or residual affinity.

(2) The chemical affinity of an atom acts uniformly from over its whole surface. Substituents must be arranged in space round the atom so as to utilise their own affinities as fully as possible (compare Claus, Le Bel, Werner), leaving a minimum proportion of free to combined affinity in the molecule.

(3) The affinity value of the hydrogen atoms is approximately one-fourth of that of the carbon atom.

(4) Addition takes place, other things being equal, at that part of the molecule where the free affinity is greatest (compare Armstrong, Thiele, Werner), which holds good also for substitution, since this is preceded always by molecular addition (Armstrong, Kekulé, Werner).

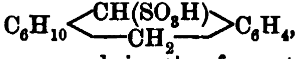
This view of the mode of action of chemical affinity, which is discussed and illustrated in the case of a number of acyclic and cyclic compounds, differs from that of Werner in that the chemical energy is considered to act from the whole surface of the atom and not from its centre of gravity, and, in so far as the equilibrium between the combined and free affinities is concerned, to follow the laws of static electricity, but is in agreement with Traube's view (this vol., ii, 205) that an atom has not individual valons (electrons), but a valon volume filled uniformly with ether, the maximum valency of the atom being determined by the stere of its valon volume. G. Y.

Hydrolysis of Benzenesulphonic Esters in Alcohol. ARTUR PRAETORIUS (*Monatsh.*, 1907, 28, 767—802).—The hydrolysis of methyl benzenesulphonate in aqueous acid and alkaline solutions, and in presence of halogen anions, has been studied previously (Abstr., 1905, i, 186; 1906, i, 736), and the results obtained shown to agree with Wegschieder's formula for the hydrolysis of esters (Abstr., 1902, ii, 493). As in these experiments, water was present always in excess, the author has now investigated the hydrolysis of methyl and ethyl benzenesulphonates in alcoholic solutions containing only limited amounts of water. Determinations of the rate of hydrolysis of the sulphonic esters in methyl- and ethyl-alcoholic solutions containing 0—10% of water, show that the action of the alcohol and the water is proportional to their concentrations. Methyl benzenesulphonate reacts with alcohol and water more easily than does the ethyl ester. Both esters are hydrolysed more rapidly by methyl than by ethyl alcohol, and react more easily with water in methyl- than in ethyl-alcoholic solution. The relation of the action of the water to that of the alcohol is independent of the ester.

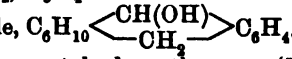
The hydrolysis of benzenesulphonic esters by means of alkalis in aqueous-ethyl alcoholic solution is a reaction of the hydroxyl and ethoxyl ions; hence only the dissociated part, termed the "active mass," of the alkali takes part in the reaction. The addition of water, on the one hand, increases this active mass, as is shown by the conductivity, but, on the other, by altering the nature of the medium, leads to changes in the constant of velocity of hydrolysis.

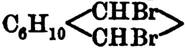
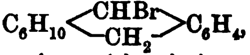
It is found that whilst the rate of hydrolysis may be accelerated by addition of traces of water, it is retarded by the presence of large amounts. The relation between the water-alcohol concentration and the constant of hydrolysis by means of alkalis is represented by the expression: $K_2' = [e_a.n_a/(n_a + n_w) + e_w.n_w/(n_a + n_w)]\,[a_a.n_a/(n_a + n_w) + a_w.n_w/(n_a + n_w)]$, in which e_a and e_w are the reactivities of the ester in alcohol and water, a_a and a_w those of the alkali in alcohol and water, and n_a and n_w the molecular concentrations of the alcohol and water respectively. In consequence of the alteration of the medium by the water, it is not possible to determine if the action of the alkali is accelerated by the addition of water according to the law of mass action. G. Y.

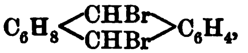
Octahydroanthracene and its Derivatives. Marcel Godchot (*Bull. Soc. chim.*, 1907, [iv], 1, 701—710. Compare this vol., i, 308).—When octahydroanthracene is heated with concentrated sulphuric acid, it yields *octahydroanthracene-9-sulphonic acid*,



$$C_6H_{10}<\begin{matrix}CH(SO_3H)\\CH_2\end{matrix}>C_6H_4,$$

which could not be prepared in the free state; its *barium* salt, $(C_{14}H_{17}SO_3)_2Ba,2H_2O$, is readily soluble in water. When fused with alkali hydroxide, sodium octahydroanthracenesulphonate yields *β-hexahydroanthracene*, $C_6H_{10}:(C_2H_2):C_6H_4$, which can also be obtained by dehydrating octahydroanthranole,  $C_6H_{10}<\begin{matrix}CH(OH)\\CH_2\end{matrix}>C_6H_4$.

The action of bromine (2 mols.) on octahydroanthracene (1 mol.) in carbon disulphide or acetic acid at the ordinary temperature yields: (1) 9:10-*Dibromo-octahydroanthracene*,  $C_6H_{10}<\begin{matrix}CHBr\\CHBr\end{matrix}>C_6H_4$, which may also be obtained by the addition of bromine to β-hexahydroanthracene; it crystallises from ethyl acetate in large, colourless needles, m. p. 194° (corr.), dissolves readily in benzene or chloroform, and sparingly in alcohol or acetic acid, and does not lose its bromine when treated with aqueous or alcoholic potassium hydroxide at 250°. (2) 9-*Bromo-octahydroanthracene*,  $C_6H_{10}<\begin{matrix}CHBr\\CH_2\end{matrix}>C_6H_4$, which has a yellow colour, gives a red coloration with picric acid, and loses hydrogen bromide with formation of β-hexahydroanthracene when distilled in a vacuum or when heated with aqueous or alcoholic potassium hydroxide at 150°; on oxidation with chromic acid in acetic acid solution, it yields β-dihydro-oxanthranol. (3) 9:10-*Di-*

bromohexahydroanthracene,  $C_6H_8<\begin{smallmatrix}CHBr\\CHBr\end{smallmatrix}>C_6H_4$, which crystallises from ethyl acetate in slender, faintly-yellow needles, m. p. 163° (corr.), and gives blue, fluorescent solutions, especially in acetic acid.

The action of chlorine (2 mols.) on octahydroanthracene (1 mol.) in carbon disulphide or acetic acid yields the following chloro-derivatives analogous to the above bromo-compounds: 9 : 10-*dichloro-octahydroanthracene*, $C_{14}H_{16}Cl_2$, crystallises from ethyl acetate in large, colourless needles, m. p. 192° (corr.). 9-*Chloro-octahydroanthracene*, $C_{14}H_{17}Cl$, is obtained as a syrupy liquid. 9 : 10-*Dichlorohexahydroanthracene*, $C_{14}H_{14}Cl_2$, crystallises from ethyl acetate in slender, colourless needles, m. p. 159° (corr.). The transformations of these chloro-compounds are similar to those of the corresponding bromo-derivatives.

Oxidation of octahydroanthracene by means of chromic acid yields hexahydroanthrone and a small proportion of β-dihydro-oxanthranol. Concentrated nitric acid attacks octahydroanthracene vigorously, but no crystalline product has been isolated. T. H. P.

Action of Bromine in Presence of Aluminium Bromide on Thiophenol and on Phenyl Disulphide. FÉLIX TABOURY (*Bull. Soc. chim.*, 1907, [iv], 1, 741—742. Compare Bodroux, Abstr., 1898, i, 641).—The action of bromine in presence of aluminium bromide on either thiophenol or phenyl disulphide at 0° yields *s-hexabromophenyl disulphide*, $C_6H_2Br_3{\cdot}S{\cdot}S{\cdot}C_6H_2Br_3$, which crystallises from chloroform in white needles, m. p. 178—180°. T. H. P.

Phenyl Chlorothiolcarbonates. II. HENRI RIVIER (*Bull. Soc. chim.*, 1907, [iv], 1, 733—740. Compare Abstr., 1906, i, 947).—*Phenyl chlorothiolcarbonate*, $COCl{\cdot}SPh$, prepared by the interaction of lead thiophenoxide (1 mol.) and carbonyl chloride (2 mols.) in toluene solution, is a colourless oil with a characteristic odour, b. p. 104°/13 mm., 150°/22 mm., and 225—227°/724 mm. (decomp.); D_4^{15} 1·285.

Ethyl phenylthiolcarbonate, $CO_2Et{\cdot}SPh$, which was obtained in an impure condition by Otto and Rössing (Abstr., 1886, 692), may be prepared by heating phenyl chlorothiolcarbonate in alcoholic solution, and is a colourless liquid with an ethereal odour, b. p. 252—253°/740 mm., 130°/16 mm., and 135°/20 mm., m. p. 6°, D_4^{15} 1·139.

Phenyl phenylthiolcarbonate, $CO_2Ph{\cdot}SPh$, prepared by the action of phenyl chlorothiolcarbonate (1 mol.) on a solution of phenol (1 mol.) in the equivalent quantity of sodium hydroxide, crystallises from alcohol in slender, colourless needles, m. p. 56°.

Phenyl dithiolcarbonate, $CO(SPh)_2$, prepared by the action of sodium or lead thiophenoxide on phenyl chlorothiolcarbonate, forms colourless crystals, m. p. 41°, and dissolves readily in alcohol.

Phenyl thiolcarbamate, $NH_2{\cdot}CO{\cdot}SPh$, obtained by gradual addition of an alcoholic solution of ammonia (2 mols.) to an ethereal solution of phenyl chlorothiolcarbonate (1 mol.), crystallises from benzene in colourless needles, m. p. 91—92°, dissolves readily in alcohol or ether, and is hydrolysed by alkali or, to a slight extent, by boiling water into ammonia, carbon dioxide, and thiophenol.

Phenyl phenylthiolcarbamate, $NHPh{\cdot}CO{\cdot}SPh$, obtained by the interaction of phenyl chlorothiolcarbonate and aniline (2 mols.) in alcoholic solution, has m. p. 122—122·5°; the product, m. p. 125°, prepared by the method of Snape (Trans., 1885, **47**, 770), contains carbanilide. Phenyl phenylthiolcarbamate dissociates on heating into phenylcarbimide and thiophenol. When boiled in alcoholic solution or when treated with alkali, it decomposes according to the equation: $NHPh{\cdot}CO{\cdot}SPh + H_2O = NH_2Ph + CO_2 + PhSH$.

Phenyl phenylmethylthiolcarbamate, $NMePh{\cdot}CO{\cdot}SPh$, obtained by the action of phenyl chlorothiolcarbonate on methylaniline, forms rhombic prisms, m. p. 66—66·5°, and is soluble in alcohol. *Phenyl ethylphenylthiolcarbamate*, $NEtPh{\cdot}CO{\cdot}SPh$, crystallises in plates, m. p. 96·5—97°. These compounds are not decomposed by boiling with alcohol, or by dilute acid, or alkali.

Phenyl chlorodithiocarbonate, $Cl{\cdot}CS{\cdot}SPh$, prepared by the interaction of thiocarbonyl chloride (1 mol.), thiophenol (1 mol.), and aqueous sodium hydroxide (1 mol.) in chloroform solution, is an orange-red oil with a pungent odour, b. p. 135°/15 mm., D_4^{15} 1·331, and dissolves in organic solvents. When boiled with alcohol, it is converted into phenyl ethylxanthate, which was prepared by Leuckart (Abstr., 1890, 603) in an impure state and forms a pale yellow liquid having a characteristic odour; b. p. 155°/16 mm. or 171°/35 mm., D_4^{15} 1·168. The action of phenol in alcoholic potassium hydroxide solution on phenyl chlorodithiocarbonate yields phenyl thionthiolcarbonate, $SPh{\cdot}CS{\cdot}OPh$, m. p. 51°, described as diphenyl dithiocarbonate in the first portion of this paper (*loc. cit.*). Sodium or lead thiophenoxide converts phenyl dithiocarbonate into *phenyl trithiocarbonate*, CS_3Ph_2, which crystallises from alcohol in deep yellow leaflets, m. p. 95·5—95·7°, and is soluble in ether. The action of alcoholic ammonia on an ethereal solution of phenyl chlorodithiocarbonate proceeds as follows: $Cl{\cdot}CS{\cdot}SPh + 2NH_3 = NH_4Cl + NH_2{\cdot}CS{\cdot}SPh$; $NH_2{\cdot}CS{\cdot}SPh + NH_3 = NH_4CNS + PhSH$; $PhSH + NH_2{\cdot}CS{\cdot}SPh = NH_3 + CS_3Ph_2$.

Phenyl phenyldithiocarbamate, $NHPh{\cdot}CS{\cdot}SPh$, obtained by the interaction of phenyl chlorodithiocarbonate (1 mol.) and aniline (2 mols.) in alcoholic solution, separates from alcohol in colourless crystals, m. p. 104—106°; at its melting point it dissociates to a slight extent into thiophenol and phenylthiocarbimide, from which products it may be prepared. *Phenyl phenylmethyldithiocarbamate*, $NMePh{\cdot}CS{\cdot}SPh$, prepared from phenyl chlorodithiocarbonate and methylaniline, forms colourless crystals, m. p. 99·5°, dissolves in alcohol, and is turned yellow by the action of light. Phenyl phenylethyldithiocarbamate, similarly prepared, has been described by Billeter and Strohl (Abstr., 1888, 364). T. H. P.

Structure of Nitrosothymol Dyes. Derivatives of Thymol Benzyl Ether. BORIS SOLONINA (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 751—759. Compare Abstr., 1905, i, 197).—Thymol benzyl ether, prepared by the action of benzyl chloride on thymol in the presence of sodium ethoxide, is of a pale colour, b. p. 221—223°/35 mm.; D_{18}^{18} 1·0063, n_D^{20} 1·5511. When dissolved in cold glacial acetic acid and treated with a cooled solution of nitric acid (D 1·40) in the same solvent, a variety of colours are produced and finally a dark blue solution is formed from which the *oxonium nitrate*,

$$CH_2Ph\cdot O(NO_3){:}C_6H_2MePr^{\beta}{:}NO\cdot C_6H_2MePr^{\beta}\cdot OH(NO_3)\cdot CH_2Ph,$$

m. p. – 68°, separates in bright copper-coloured crystals; when powdered, it appears dark blue and has m. p. – 62°. It is fairly stable in a vacuum, but decomposes when heated, forming a red substance. When an alkali is added to its acid solution, it turns yellow, but becomes blue again on addition of acid, but very soon decomposes, forming a red substance. Hydrogen sulphide, sulphur dioxide, and stannous chloride reduce it, forming *dibenzyl*-p-*dithymolylamine*,

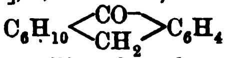
$$NH(C_6H_2MePr^{\beta}\cdot O\cdot CH_2Ph)_2,$$

m. p. 141·5°, analogous in properties to its ethyl, methyl, and butyl homologues; the *hydrochloride* has m. p. 142°. When oxidised with ferric chloride, the amine is converted into p-*thymoquinone thymolimide benzyl ether*, $O{:}C_6H_2MePr^{\beta}{:}N\cdot C_6H_2MePr^{\beta}\cdot O\cdot CH_2Ph$, m. p. 81·5°, which is similar in properties to the corresponding ethyl compound, and is reduced quantitatively to dithymolylamine, $C_{27}H_{33}O_2N$, by stannous chloride. Z. K.

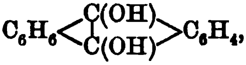
Preparation and Purification of Hydroxyanthraquinone and Hydroxynaphthaquinone Derivatives and especially of Juglone and Emodin. R. Combes (*Bull. Soc. chim.*, 1907, [iv], 1, 800—816).—The reaction with nickel acetate previously described (Abstr., 1906, ii, 118, and this vol., ii, 411) is utilised for the isolation of these hydroxyquinones. The fresh pericarp of the walnut is used as a source of juglone, which is extracted by means of ether, freed from chlorophyll and other impurities by solution in benzene, and finally purified by conversion into the nickel compound, from which it is regenerated by means of acetic acid. From the aqueous solution so obtained, the juglone is extracted by ether or chloroform and finally crystallised from benzene. In old walnut pericarps, which have become brown, the juglone has been transformed into hydrojuglone, so that in preparing the former from such material the crude product recovered from the first solution in benzene is re-dissolved in ether and shaken with chromium mixture as suggested by Bernthsen and Semper (Abstr., 1885, 546). The oxidised product is freed from traces of adherent chromium compounds by repeatedly washing the solution in ether with water and is purified as before. The above methods can be applied generally for the isolation of hydroxynaphthaquinones.

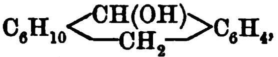
Alder bark collected in May is employed as a source of emodin. The powdered bark is extracted with a dilute solution of sodium hydroxide and the crude emodin, obtained on acidifying this solution with dilute hydrochloric acid, treated with an aqueous solution of nickel acetate, containing calcium carbonate in suspension, whereby the soluble nickel compound of emodin is formed. Dilute hydrochloric acid is added in excess to this solution, when emodin slowly crystallises out, separation being complete after several days. The crystals are purified by washing with 10% hydrochloric acid. This process is a general one for the isolation of hydroxyanthraquinones. T. A. H.

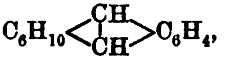
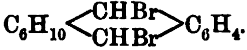
Hexahydroanthrone and its Derivatives. MARCEL GODCHOT (*Bull. Soc. chim.*, 1907, [iv], 1, 710—719).—Hexahydroanthrone,

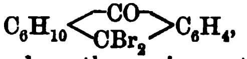


$$C_6H_{10}<\genfrac{}{}{0pt}{}{CO}{CH_2}>C_6H_4$$

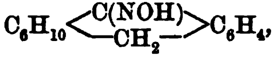
(see this vol., i, 837), crystallises in pale yellow, hard needles, m. p. 45·5°, b. p. 222—225°/25 mm., dissolves readily in ether, alcohol, benzene, or acetic acid, gives a red coloration with concentrated sulphuric acid, and reduces ammoniacal silver nitrate and alkaline copper solutions, but does not combine with sodium hydrogen sulphite. Oxidation with chromic acid in acetic acid solution at 100° converts it into dihydro-9-hydroxyanthranol,  $C_6H_6<\genfrac{}{}{0pt}{}{C(OH)}{C(OH)}>C_6H_4$, and a small proportion of anthraquinone.

Octahydroanthranol,  $C_6H_{10}<\genfrac{}{}{0pt}{}{CH(OH)}{CH_2}>C_6H_4$, prepared by reducing hexahydroanthrone with sodium and absolute alcohol, crystallises from aqueous alcohol in rosettes of faintly yellow needles, m. p. 81—82°, dissolves readily in the ordinary solvents, and gives a red coloration with picric acid. On distillation, even in a vacuum, it loses water, forming β-hexahydroanthracene (see below). Its *phenylurethane* derivative, $C_{14}H_{17}O\cdot CO\cdot NHPh$, crystallises from acetone in colourless needles, m. p. 151—152°.

β-Hexahydroanthracene,  $C_6H_{10}<\genfrac{}{}{0pt}{}{CH}{CH}>C_6H_4$, also prepared by the action of dehydrating agents on octahydroanthranol, crystallises in colourless plates, m. p. 66·5°, b. p. 303—306°, and dissolves readily in alcohol, acetic acid, or benzene, giving solutions exhibiting blue fluorescence. Oxidation with chromic acid in acetic acid solution converts it into dihydro-9-hydroxyanthranol. It takes up Br_2 (or Cl_2), yielding  $C_6H_{10}<\genfrac{}{}{0pt}{}{CHBr}{CHBr}>C_6H_4$.

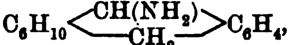
Dibromohexahydroanthrone,  $C_6H_{10}<\genfrac{}{}{0pt}{}{CO}{CBr_2}>C_6H_4$, prepared by the action of bromine on hexahydroanthrone in acetic acid or carbon disulphide, crystallises from acetone in colourless plates, m. p. 123—124°, dissolves readily in most of the ordinary solvents, and when oxidised with chromic acid in acetic acid solution yields only a small proportion of anthraquinone, most of the compound undergoing complete oxidation. It does not yield an oxime or a semicarbazone.

Hexahydroanthronesemicarbazone, $C_{14}H_{16}:N\cdot CO\cdot NH\cdot NH_2$, crystallises from aqueous alcohol in faintly yellow needles, m. p. 250°, and dissolves sparingly in alcohol, ether, or acetone. The *oxime*,



$$C_6H_{10}<\genfrac{}{}{0pt}{}{C(NOH)}{CH_2}>C_6H_4,$$

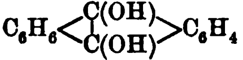
crystallises from alcohol in colourless needles, m. p. 143°.

γ-Octahydroanthramine,  $C_6H_{10}<\genfrac{}{}{0pt}{}{CH(NH_2)}{CH_2}>C_6H_4$, prepared by reducing the preceding oxime, is a yellow, strongly basic liquid, b. p.

182°/12 mm. The *hydrochloride*, $C_{14}N_{19}N,HCl$, m. p. 188°; *picrate*, $C_{14}H_{19}N,C_6H_3O_7N_3$, m. p. 212°, and *acetyl* derivative, $C_{14}H_{17}\cdot NHAc$, m. p. 183°, were prepared. T. H. P.

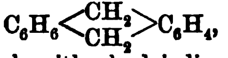
Dihydro-9-hydroxyanthranol and its Derivatives. MARCEL GODCHOT

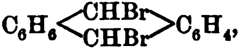
(*Bull. Soc. chim.*, 1907, [iv], 1, 719—724. Compare preceding abstracts).—*Dihydro-9-hydroxyanthranol*,



$$C_6H_6\left<\begin{matrix}C(OH)\\ |\\ C(OH)\end{matrix}\right>C_6H_4$$

(compare Schulze, Abstr., 1886, 247), crystallises from ethyl acetate in golden-yellow, prismatic needles, m. p. 158·5°, dissolves readily in benzene or its homologues or alcohol, gives a red coloration with sulphuric acid, and a deep red colour with a trace of alkali. Its *diacetyl* derivative, $C_{14}H_{10}(OAc)_2$, m. p. 220°, gives solutions exhibiting a blue fluorescence, and its *dibenzoyl* compound, $C_{14}H_{10}(OBz)_2$, has m. p. 255° (partially decomp.). When subjected to the prolonged action of chromic acid, it yields a small proportion of anthraquinone.

γ-Tetrahydroanthracene,  $C_6H_6\left<\begin{matrix}CH_2\\ CH_2\end{matrix}\right>C_6H_4$, prepared by reducing dihydro-9-hydroxyanthranol with hydriodic acid, crystallises from alcohol in colourless plates, m. p. 101°. Its *dibromo*-derivative,



$$C_6H_6\left<\begin{matrix}CHBr\\ CHBr\end{matrix}\right>C_6H_4,$$

crystallises from ethyl acetate in large, faintly yellow needles, m. p. 169°, dissolves readily in benzene, does not give up its bromine to aqueous or alcoholic potassium hydroxide at 200°, and gives dihydro-9-hydroxyanthranol when treated with chromic acid in acetic acid solution. T. H. P.

Electrolytic Reduction of the Three Isomeric Nitrobenzylsulphonic Acids. L. WEISS and K. REITER

(*Annalen*, 1907, 355, 175—195).—The experiments have been performed in aqueous, alcoholic, or aqueous-alcoholic solutions in a divided cell with lead, nickel, or platinum cathodes, the completion of the reduction being ascertained by comparing the indications of a water-voltameter in the circuit with the amount of gas collected in a eudiometer at the cathode. In alkaline solution, sodium *o*- and *p*-nitrobenzylsulphonates are converted into the corresponding azobenzyldisulphonates; the *m*-isomeride does not give definite results. In faintly acid solution, the three isomerides are reduced through the hydroxylamine derivatives to the aminosulphonic acids. In strongly acid solution, the *o*- and *m*-nitrosulphonates are converted into the hydroxylamine derivatives, which are then transformed into the isomeric aminohydroxysulphonic acids; *p*-hydroxylaminobenzylsulphonic acid, which cannot undergo the preceding transformation, is reduced to the aminosulphonic acid by the addition of alcohol or by the prolonged action of the electric current.

A table is given which states the composition of the solution, the nature and area of the cathode, the current strength, the voltage, and the yield. C. S.

Piperidides. ANTOINE P. N. FRANCHIMONT, WILLEM VAN RIJN, and HERMANN FRIEDMANN (*Rec. trav. chim.*, 1907, **26**, 228—239).—The authors have prepared various piperidides and have subjected them to the action of concentrated nitric acid. It is found that the piperidides of the nitrobenzoic acids and of 2 : 4- and 3 : 5-dinitrobenzoic acids are not attacked by nitric acid at the ordinary temperature, whilst those of succinic and sulphuric acid yield nitropiperidine (compare Franchimont and Erp, Abstr., 1896, i, 602; Franchimont and Taverne, *ibid.*).

Malonylpiperidide, $C_{13}H_{22}O_2N_2$, prepared by the action of ethyl malonate (1 mol.) on piperidine (rather more than 2 mols.), separates from light petroleum in crystals, m. p. 57°.

Succinylpiperidide, $C_{14}H_{24}O_2N_2$, prepared by the interaction of succinyl chloride (1 mol.) and piperidine (4 mols.), separates from light petroleum in crystals, m. p. 70°.

o-*Nitrobenzoylpiperidide*, $C_{12}H_{14}O_3N_2$, prepared by the action of *o*-nitrobenzoyl chloride on piperidine, crystallises from alcohol in pale yellow, rectangular, triclinic plates [F. M. JAEGER, $a : b : c = 1\cdot3444 : 1 : 0\cdot9672$; $\alpha = 101°34'$, $\beta = 95°59\frac{1}{3}'$, $\gamma = 70°36'$], m. p. 56°, D^{15} 1·345.

p-*Nitrobenzopiperidide*, $C_{12}H_{14}O_3N_2$, separates from alcohol in faintly yellow, rhombic crystals [F. M. JAEGER, $a : b : c = 1\cdot1128 : 1 : 0\cdot9620$], m. p. 120·5°, D^{15} 1·310.

The molecular volumes of *o*-, *m*-, and *p*-nitrobenzoylpiperidides are 173·97, 176·70, and 179·40 respectively, the differences being 2·73 and 2·70; the molecular volume is hence greatest for the crystals exhibiting the lowest symmetry.

2 : 4-*Dinitrobenzoylpiperidide*, $C_{12}H_{13}O_5N_3$, crystallises from alcohol in slender, pale yellow needles, m. p. 159°.

3 : 5-*Dinitrobenzoylpiperidide*, $C_{12}H_{13}O_5N_3$, crystallises from alcohol in shining scales, m. p. 147°.

T. H. P.

Arylanthranilic Acids. FRITZ ULLMANN (*Annalen*, 1907, **355**, 312—358).—In connexion with work previously published with Sponagel (Abstr., 1905, i, 644), the author observed that phenylanthranilic acid is formed when copper powder is added to a boiling solution of *o*-chlorobenzoic acid in aniline. This action has now been further studied. The condensation between *o*-chlorobenzoic acid and aniline takes place the more readily the higher the temperature; it is noted, however, that at high temperatures the phenylanthranilic acid formed is decomposed into diphenylamine and carbon dioxide, so that the heating must not be continued too long. Better results are obtained when potassium carbonate is added to the reaction mixture, since not only is potassium phenylanthranilate stable at high temperatures, but the hydrogen chloride formed is neutralised. In some cases, where vessels of copper or of iron were used, the addition of copper powder was not necessary.

The action of various catalysts in promoting the condensation was studied. Salts of iron, nickel, platinum, and zinc act as catalysts, whilst salts of manganese and tin do not. The best catalyst is copper, a trace of which suffices.

The condensation between aniline and *o*-bromobenzoic acid or *o*-iodobenzoic acid takes place without the addition of a catalyst.

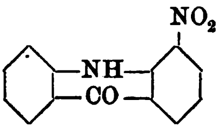
The action was extended to the preparation of substituted phenylanthranilic acids and is general for the preparation of arylanthranilic acids, since other aromatic amines may be substituted for aniline. In order to obtain good yields of the latter acids, the addition of amyl alcohol or nitrobenzene to the mixture of amine and acid is of service.

The arylanthranilic acids described are of interest on account of the ease with which they are converted into acridone derivatives; they may also be used for the preparation of unsymmetrical diphenylamine derivatives. The acridone derivatives prepared were examined with respect to their fluorescent properties; halogen acridones fluoresce like acridone itself, but, when a nitro-group is present in the acridone, there is no fluorescence. 2- and 4-Aminoacridones exhibit strong fluorescence in alcoholic solution, whilst 1-aminoacridone does not fluoresce in the same solvent. When hydrochloric acid is added to the alcoholic solution of each one of these aminoacridones, the solution of the 1-amino-compound fluoresces and the others do not. The alcoholic solutions of 2- and 4-hydroxyacridones exhibit a blue fluorescence, whilst the yellow solutions in dilute alkalis exhibit a green fluorescence.

[With Paul Dieterle.]—The preparation of phenylanthranilic acid and the influence of various catalysts are described in detail.

[With Walter Bader.]—*o*-Tolylanthranilic acid, obtained from *o*-chlorobenzoic acid, *o*-toluidine, potassium carbonate, and copper powder, crystallises from benzene in colourless leaflets, m. p. 185° (Locher, Abstr., 1894, i, 530, gives 179°). When heated at 230—250°, it is converted into phenyl-*o*-toluidine. *m-Tolylanthranilic acid*, prepared from *o*-chlorobenzoic acid and *m*-toluidine in a similar manner, separates from benzene in colourless leaflets, m. p. 139°, and, when distilled, is converted into phenyl-*m*-toluidine. *p*-Tolylanthranilic acid was similarly prepared, m. p. 196° (Kahn gives 191·5°); it is readily converted into phenyl-*p*-toluidine. 2 : 4-Xylylanthranilic acid was also prepared, m. p. 187° (Kaufmann gives 182°); phenyl-2 : 4-xylylamine has m. p. 44° (Girard and Vogt give m. p. 52°).

2′-Nitrodiphenylamine-2-carboxylic acid, $NO_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot CO_2H$, prepared from potassium *o*-chlorobenzoate, *o*-nitroaniline, copper acetate, potassium carbonate, and amyl alcohol, crystallises from benzene in dark yellow, glistening needles, m. p. 219°. Its solution in concentrated sulphuric acid is yellow and becomes green on the addition of nitric acid. When heated at 100° with concentrated sulphuric acid, it forms 1-*nitroacridone*, which separates from toluene in glistening, orange-red needles, m. p. 262°; its solution in concentrated sulphuric acid is yellowish-brown and, when its alcoholic solution is boiled with sodium sulphide, 1-*aminoacridone*, $C_{13}H_{10}ON_2$, is formed, which crystallises from alcohol in dark yellow needles, m. p. 355° (decomp.). The solution of the latter compound in concentrated sulphuric acid is yellowish-green and exhibits a blue fluorescence.



3′-*Nitrodiphenylamine-2-carboxylic acid*, $C_{13}H_{10}O_4N_2$, obtained by the condensation of *m*-nitroaniline with *o*-chlorobenzoic acid, crystallises from alcohol in yellow needles, m. p. 218°. Its solution in concentrated sulphuric acid is yellow and, on the addition of nitric acid, becomes brown and then green. On reduction, it forms 3′-*aminodiphenylamine-2-carboxylic acid*, $C_{13}H_{12}O_2N_2$, which crystallises from toluene in colourless needles, m. p. 166° (decomp.); when warmed with concentrated sulphuric acid, a green fluorescence is observed and, on the addition of nitric acid, the solution becomes first brownish-red and then dirty green. When heated at 215—220°, 3′-nitrodiphenylamine-2-carboxylic acid forms 3-*nitrodiphenylamine*, which separates from dilute alcohol in red leaflets, m. p. 114°, and forms an almost colourless solution in concentrated sulphuric acid which, on the addition of nitric acid, assumes first a violet and then a brown tint. Concentrated sulphuric acid converts 3′-nitrodiphenylamine-2-carboxylic acid into 4-*nitroacridone*, which separates from nitrobenzene in yellow needles and with concentrated sulphuric acid forms a yellow solution which does not fluoresce. 4-*Aminoacridone* crystallises from alcohol in yellow needles, m. p. 285°; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence.

4′-*Aminodiphenylamine-2-carboxylic acid*,

$$NH_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot CO_2H,$$

prepared by the condensation of *o*-chlorobenzoic acid with *p*-phenylenediamine, separates from xylene in yellow needles, m. p. 205° (decomp.). Its solution in dilute hydrochloric acid assumes a faintly violet tint on exposure to the air. 3-*Aminoacridone* crystallises from alcohol in yellow needles, which melt indefinitely at 298°. Its solution in alcohol or in acetone is yellow and exhibits a green fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

[With ERNST TEDESCO.]—Monohalogen-anilines condense readily with *o*-chlorobenzoic acid. The less basic dichloroaniline also condenses, but tribromoaniline does not.

2′-*Chlorodiphenylamine-2-carboxylic acid*, $C_6H_4Cl\cdot NH\cdot C_6H_4\cdot CO_2H$, prepared by heating a mixture of potassium *o*-chlorobenzoate, *o*-chloroaniline, amyl alcohol, and copper powder, crystallises from benzene in white needles, m. p. 192°. 1-*Chloroacridone* crystallises from glacial acetic acid in bright yellow needles, m. p. over 360°. Its alcoholic solution exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid has a bluish-green fluorescence. 3′-*Chlorodiphenylamine-2-carboxylic acid* crystallises from benzene in colourless needles, m. p. 167°, and when heated at 250—260° until the evolution of carbon dioxide ceases it forms 3-*chlorodiphenylamine*, an oil, b. p. 335—336°/724 mm.

4-*Chloroacridone* crystallises from glacial acetic acid or nitrobenzene in yellow needles, m. p. over 360°. Its alcoholic solution exhibits a weak blue fluorescence.

4′-*Chlorodiphenylamine-2-carboxylic acid*, obtained by the usual method from *p*-chloroaniline, forms yellow needles, m. p. 177°. 3-*Chloroacridone* forms yellow needles, m. p. over 360°. Its alcoholic solution is faintly yellow with a bluish-violet fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

4-Chlorodiphenylamine, obtained from 4′-chlorodiphenylamine-2-carboxylic acid as usual, has m. p. 74° and b. p. 334—335°/726 mm.

2′ : 4′-*Dichlorodiphenylamine-2-carboxylic acid*, prepared by the condensation of dichloroaniline with potassium *o*-chlorobenzoate, separates from glacial acetic acid in yellow needles, m. p. 249°.

1 : 3-*Dichloroacridone* crystallises from glacial acetic acid in yellow needles, m. p. over 360°. Its solution in glacial acetic acid is yellow and exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid is yellow and exhibits a blue fluorescence.

2 : 4-*Dichlorodiphenylamine* separates from dilute alcohol in needles, m. p. 64°; its solution in concentrated sulphuric acid is colourless, but, on the addition of nitric acid, becomes first violet and then reddish-brown. 4′-*Bromodiphenylamine*-1-*carboxylic acid* separates from a mixture of benzene and light petroleum in glistening leaflets, m. p. 185°. 3-*Bromoacridone* crystallises from glacial acetic acid in bright yellow needles, m. p. over 360°; its alcoholic solution is faintly yellow and exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

[With HERMANN KIPPER.]—The condensation of potassium *o*-chlorobenzoate with *o*-aminophenol gives only a 40% yield. With *o*-anisidine, the yield is 85% when amyl alcohol is used as the solvent. Good yields are also obtained with *m*-anisidine and *p*-phenetidine respectively.

2-*Hydroxydiphenylamine*-2-*carboxylic acid*,

$$OH\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot CO_2H,$$

crystallises from dilute alcohol in glistening needles, m. p. 190°.

2-*Methoxydiphenylamine-2-carboxylic acid*, obtained from *o*-anisidine, crystallises from benzene in colourless needles, m. p. 176°. 2-*Methoxydiphenylamine*, obtained by heating the preceding compound at 240—260°, is a colourless liquid, b. p. 325—326°/732 mm.; it becomes brown on exposure to the air. 1-*Methoxyacridone* separates from 50% acetic acid in faintly yellow needles, m. p. 293°; its alcoholic solution is faintly yellow and exhibits a bluish-violet fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

1-*Hydroxyacridone*, obtained either by the usual method from 2′-hydroxydiphenylamine-2-carboxylic acid or by the action of aluminium chloride on 1-methoxyacridone, using xylene as solvent, crystallises from dilute acetic acid in yellow needles, which sinter at 290° and melt at 300°. Its alcoholic solution exhibits a blue fluorescence; its solution in dilute aqueous sodium hydroxide is yellow; its solution in concentrated sulphuric acid is yellowish-brown and exhibits a green fluorescence.

3′-*Methoxydiphenylamine*-2-*carboxylic acid*, obtained from *m*-anisidine, separates from a mixture of benzene and light petrolenm in colourless needles, m. p. 132°. 4′-*Ethoxydiphenylamine-2-carboxylic acid*, obtained from *p*-phenetidine, crystallises from dilute acetic acid in colourless needles, m. p. 209°. 3-Hydroxyacridone, obtained from the preceding compound, crystallises from alcohol in yellow needles, m. p. 345—350° (indefinite); its solution in alcohol is yellow and exhibits a bluish-green fluorescence; its solution in concentrated sulphuric acid is faintly yellow and exhibits a green fluorescence.

[With **Georges Rasetti.**]—The condensation of β-naphthylamine with *o*-chlorobenzoic acid proceeds better than that of α-naphthylamine. The corresponding naphthacridones cannot readily be obtained by the sulphuric acid method, since the naphthalene nucleus undergoes sulphonation; the aluminium chloride method, however, may conveniently be used.

α-Naphthylaniline-2-carboxylic acid, $C_{10}H_7 \cdot NH \cdot C_6H_4 \cdot CO_2H$, separates from a mixture of benzene and light petroleum in colourless, glistening leaflets, m. p. 208°. When its solution in concentrated sulphuric acid is warmed, it becomes yellow and exhibits a bluish-green fluorescence.

2 : 1-*Naphthacridone* is prepared by adding phosphorus pentachloride to a solution of the preceding acid in thiophen-free benzene, warming until the solution of hydrogen chloride ceases and then heating with aluminium chloride; it crystallises from pyridine in faintly yellow needles, m. p. over 360°; its solution in concentrated sulphuric acid exhibits a blue fluorescence. When distilled with zinc dust, it forms the corresponding naphthacridine.

β-Naphthylaniline-2-carboxylic acid crystallises from acetone in white, glistening needles, m. p. 212°. 1 : 2-*Naphthacridone* forms orange-yellow needles, m. p. over 360°; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence; on reduction with zinc dust, the corresponding naphthacridine is formed.

[With **Heinrich Hoz.**]—*o*-Chlorobenzoic acid readily condenses with aminobenzoic acids to form diphenylaminedicarboxylic acids, which may be converted into acridonecarboxylic acids.

Diphenylamine-2 : 2′-dicarboxylic acid, $CO_2H \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot CO_2H$, obtained either from *o*-chlorobenzoic acid and anthranilic acid or by the action of ammonia on *o*-chlorobenzoic acid, in which case anthranilic acid is the primary product, crystallises from alcohol in colourless crystals, m. p. 295° (decomp.).

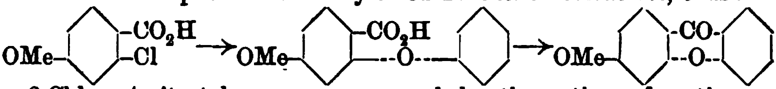
Acridone-1-carboxylic acid, $C_{14}H_9O_3N$, separates from alcohol in dark yellow needles, m. p. 325° (decomp.); its solution in alkalis is yellow and exhibits a blue fluorescence; its solution in concentrated sulphuric acid exhibits a green fluorescence. Its *methyl ester* crystallises from methyl alcohol in yellow needles, m. p. 172°; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

Diphenylamine-2 : 3′-dicarboxylic acid crystallises from alcohol in faintly brown needles, m. p. 296° (decomp.); its solution in concentrated sulphuric acid exhibits a blue fluorescence. *Diphenylamine-2 : 4′-dicarboxylic acid* forms colourless needles, m. p. 290° (decomp.).

Acridone-3-carboxylic acid forms a faintly yellow, crystalline powder, m. p. above 350°; its alcoholic solution exhibits a blue fluorescence; its solution in concentrated sulphuric acid is yellow and exhibits a bluish-green fluorescence. Its *methyl ester* forms almost colourless needles, m. p. 339°; its solution in alcohol is faintly yellow and exhibits a blue fluorescence. A. McK.

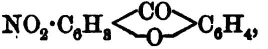
Transformations of Substituted *o*-Chlorobenzoic Acids in the Presence of Copper. Fritz Ullmann and Carl Wagner (*Annalen*, 1907, **355**, 359—371. Compare preceding abstract).—The authors have studied the interaction of substituted *o*-chlorobenzoic acids and amines in the presence of copper, when substituted diphenylamine-*o*-carboxylic acids were formed, which were then converted into the corresponding acridones.

Derivatives of salicylic acid phenyl ether were also formed by means of alkali phenoxides and yielded xanthone derivatives, thus:



2-Chloro-4-nitrotoluene was prepared by the action of antimony pentachloride on *p*-nitrotoluene and from 4-nitro-2-toluidine by Sandmeyer's method. When oxidised by potassium permanganate, it is converted into 2-chloro-4-nitrobenzoic acid, which, when heated with soda lime, water, and a trace of copper powder at 160—170° for six hours, is converted into 4-*nitrosalicylic acid*; the latter crystallises from water in almost colourless, felted needles, m. p. 226°, and gives a red coloration with ferric chloride.

When 2-chloro-4-nitrobenzoic acid is heated with sodium phenoxide and methyl alcohol at 180° in the presence of a trace of copper, it is converted into 5-*nitrodiphenyl ether*-2-*carboxylic acid* [4-*nitro*-2-*phenoxybenzoic acid*], $CO_2H{\cdot}C_6H_3(NO_2){\cdot}OPh$, which crystallises from benzene in almost colourless leaflets, m. p. 156°.

3-*Nitroxanthone*,  $NO_2{\cdot}C_6H_3{<}\overset{CO}{\underset{O}{\diamond}}{>}C_6H_4$, is obtained from the preceding acid either by means of sulphuric acid or by treatment of the chloride with aluminium chloride; it crystallises from dilute alcohol in faintly yellow needles, m. p. 176°; its solution in concentrated sulphuric acid is yellow and exhibits a green fluorescence. When reduced by stannous chloride, it is converted into 3-*aminoxanthone*, which separates from alcohol or toluene in faintly yellow, feathery needles, m. p. 232°; its alcoholic solution is almost colourless and exhibits a blue fluorescence which, on the addition of hydrochloric acid, becomes green.

5-*Nitrodiphenylamine*-2-*carboxylic acid*, $CO_2H{\cdot}C_6H_3(NO_2){\cdot}NHPh$, obtained by the condensation of 2-chloro-4-nitrobenzoic acid with aniline, crystallises from toluene in orange-yellow needles, m. p. 230°.

2-*Nitroacridone*, $NO_2{\cdot}C_6H_3{<}\overset{CO}{\underset{NH}{\diamond}}{>}C_6H_4$, obtained by the aluminium chloride method, crystallises from nitrobenzene or acetic acid in yellow needles, m. p. above 350°.

2:4-Dichlorobenzoic acid was prepared by the oxidation of 2:4-dichlorotoluene with potassium permanganate. 5-*Chlorodiphenylamine*-2-*carboxylic acid*, $CO_2H{\cdot}C_6H_3Cl{\cdot}NHPh$, obtained from 2:4-dichlorobenzoic acid and aniline, crystallises from benzene or dilute alcohol in yellow needles, m. p. 207°. 2-*Chloroacridone*, prepared by the aluminium chloride method, crystallises from glacial acetic acid in faintly yellow needles, m. p. over 360°; its alcoholic solution is yellow and exhibits a blue fluorescence; its solution in concentrated sulphuric acid exhibits a bluish-green fluorescence.

5-*Chlorodiphenyl ether*-2-*carboxylic* [4-*chloro*-2-*phenoxybenzoic*] *acid*, $CO_2H{\cdot}C_6H_3Cl{\cdot}OPh$, prepared from 2:4-dichlorobenzoic acid and sodium phenoxide, crystallises from dilute alcohol in colourless, glistening needles, m. p. 115°. 3-*Chloroxanthone*, obtained by the sulphuric acid method, separates from alcohol or a mixture of benzene and light petroleum in white, silky needles, m. p. 171°; its solution in concentrated sulphuric acid is faintly yellow and exhibits a bluish-green fluorescence.

2-Chloro-4-toluidine was converted, through the diazonium salt, into 2-*chloro*-p-*cresol*, C_7H_7OCl, which forms colourless needles, m. p. 55°, b. p. 229°/735 mm. When methylated by methyl sulphate, it forms 2-*chloro*-4-*methoxytoluene*, a colourless liquid, b. p. 212°. When the latter compound is oxidised with potassium permanganate, it is converted into *o*-chloroanisic acid, m. p. 208°, identical with the acid obtained by Tiemann by the oxidation of chloroanisaldehyde. It reacts with potassium phenoxide in the presence of a trace of copper to form 4-methoxy-2-phenoxybenzoic acid, glistening needles, m. p. 177°, which, with sulphuric acid, forms 3-methoxyxanthone, m. p. 129° (Dreher and Kostanecki, Abstr., 1893, i, 217, give 128·5°); the solution of the latter compound in concentrated sulphuric acid is faintly yellow and exhibits a blue fluorescence. By the action of aluminium chloride, 3-methoxyxanthone is converted into 3-hydroxyxanthone, m. p. 243°, the solution of which in concentrated sulphuric acid exhibits a greenish-blue fluorescence.

5-*Methoxydiphenylamine*-2-*carboxylic acid* separates from benzene in faintly yellow, glistening leaflets, m. p. 178°. By the action of sulphuric acid, it is converted into 3-methoxyacridone, which separates from dilute acetic acid in faintly yellow needles, m. p. 290°; the alcoholic solution of the latter compound exhibits a blue fluorescence.

A. McK.

Constitution of Greiff's Dibromoanthranilic Acid. Paul Friedländer and V. Laske (*Monatsh.*, 1907, **28**, 987—989).—Greiff's dibromoanthranilic acid, formed by the action of bromine on *o*-nitrotoluene (Abstr., 1880, 648), must be 3:5-dibromo-2-aminobenzoic acid, as if diazotised and boiled with alcohol it yields 3:5-dibromobenzoic acid, whilst its silver salt when heated decomposes, forming 2:4-dibromoaniline. The same constitution must be ascribed to the dibromoanthranilic acid obtained from dibromoisatin by Dorsch (Abstr., 1886, 359).

G. Y.

Synthesis of β-*p*-*iso*-Propylphenyl β-Hydroxypropionic Acid. G. Bronstein (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 578—587).—When cuminaldehyde reacts with ethyl bromoacetate in the presence of a zinc-copper couple, an ester is obtained which on hydrolysis with hot barium hydroxide yields *p*-*iso*-propylphenylacrylic acid,

$$C_3H_7\cdot C_6H_4\cdot CH\!:\!CH\cdot CO_2H,$$

of which the *barium*, $(C_{12}H_{13}O_2)_2Ba,7H_2O$, and *silver* salts are described. On saponifying the ester with cold barium hydroxide, the *barium* salt, $(C_{12}H_{16}O_3)_2Ba,8·5H_2O$, is obtained, which with dilute acid yields *β hydroxy*-*β*-p-iso*propylphenylpropionic acid*,

$$C_3H_7\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot CO_2H,$$

m. p. 95°. The following salts have been obtained: *silver*, *sodium*, *copper*, *zinc*, *magnesium*, *cobalt*, *nickel*, and *mercury*. When distilled with sulphuric acid, the acid loses water and yields *p-iso*propylphenyl acrylic acid; but the derivatives obtained by the substitution of alkyl groups for the hydrogen in the CH_2 group, when similarly treated, yield water, carbon dioxide, and an unsaturated hydrocarbon. These derivatives, like the parent substance, form colourless needles, more soluble in hot than in cold water. Z. K.

Formation of Phthalide. MARCEL GODCHOT (*Bull. Soc. chim.*, 1907, [iv], 1, 829—830).—When Sabatier and Senderens' method of catalytic reduction by means of nickel is applied to phthalic anhydride at 200°, phthalide is formed quantitatively. It was found to be impossible to obtain hydrophthalides by this process (compare Eykmann, this vol., i, 378). T. A. H.

Esterification of Anisic and Gallic Acids by means of Alcoholic Hydrogen Chloride. ANTON KAILAN (*Monatsh.*, 1907, **28**, 965—986. Compare Abstr., 1906, ii, 659; this vol., ii, 158, 242, 243).—A study of the rate of esterification of anisic and gallic acids by means of hydrogen chloride in alcoholic solutions containing varying amounts of water, at 25°. The method employed is that described previously (*loc. cit.*). The constant for the velocity of esterification, when calculated with the aid of the equation for unimolecular reactions, is found to increase more rapidly than the concentration of the hydrogen chloride in the case of anisic acid in all aqueous-alcoholic concentrations or of gallic acid in presence of much water, but more slowly than the hydrogen chloride concentration in the case of gallic acid in concentrated alcohol.

The relations of the velocity constants to the concentrations of the water and hydrogen chloride are represented by the expressions, for anisic acid: $1/k = -6{\cdot}11 + 40{\cdot}16/c - 0{\cdot}6127/c^2 + (-138{\cdot}9 + 101{\cdot}6/c + 15{\cdot}25/c^2)w + (-58{\cdot}1 + 128{\cdot}4/c + 1{\cdot}163/c^2)w^2$, and for gallic acid: $1/k = -3{\cdot}33 + 49{\cdot}07/c - 2{\cdot}916/c^2 + (61{\cdot}1 - 23{\cdot}40/c + 25{\cdot}02/c^2)w + (-276{\cdot}6 + 260{\cdot}6/c - 10{\cdot}02/c^2)w^2$. These expressions apply to solutions having the concentration of water, $w = 0{\cdot}03$ to $1{\cdot}3$, and of the hydrogen chloride, $c = 0{\cdot}16$ to $0{\cdot}67$.

Anisic acid is esterified more rapidly than is *p*-hydroxybenzoic acid. The esterification of gallic acid takes place more slowly than would be the case if the introduction of a hydroxyl group into a 3 : 4- or 3 : 5-dihydroxybenzoic acid had the same influence on the reaction as the substitution of hydroxyl for a hydrogen atom in benzoic or *m*- or *p*-hydroxybenzoic acid. The behaviour of anisic and gallic acid on esterification is compared with and shown to be analogous to that of the acids previously studied. G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XVI. Derivatives of Aminoterephthalic Acid. PAUL CAHN-SPEYER (*Monatsh.*, 1907, **28**, 803—817. Compare Abstr., 1906, i, 86; this vol., i, 60).—The action of an excess of hydrogen chloride on aminoterephthalic acid in boiling methyl-alcoholic solution leads to the formation of the dimethyl ester, m. p. 133—134° (126°: Ahrens, Abstr., 1886, 801), but of a limited amount of hydrogen chloride to that of 4-methyl 1-hydrogen 2-aminoterephthalate, m. p. 213°, which is formed also on prolonged heating of the acid with methyl alcohol at 100° under pressure, or by partial hydrolysis of the dimethyl ester by means of potassium hydroxide or hydrogen chloride in methyl alcoholic solution. On diazotisation and boiling in dilute sulphuric acid, this yields 4-methyl 1-hydrogen 2-hydroxyterephthalate (Wegscheider and Bittner, Abstr., 1900, i, 658). The dimethyl ester is obtained in a yield of 70% of the aminoterephthalic acid, together with small amounts of the 4-monomethyl ester, when the acid is heated with methyl alcohol and concentrated sulphuric acid. The action of boiling methyl iodide on silver aminoterephthalate leads to the formation of a mixture of the dimethyl and 4-monomethyl esters; at the ordinary temperature, only traces of the monomethyl ester are formed, whilst in the complete absence of water, the reaction does not take place (compare Wegscheider and Frankl, this vol., i, 373).

The product, m. p. 265°, obtained on treating aminoterephthalic acid with silver oxide and methyl iodide, or the potassium hydrogen salt with methyl iodide, is found now to be a mixture of methylamino- and dimethylamino-terephthalic acids (compare Süss, Abstr., 1906, i, 86).

Acetylaminoterephthalic acid crystallises in yellow needles, decomp. 355°, is not fluorescent, and is hydrolysed readily by boiling dilute sulphuric acid; the *silver*, $C_{10}H_7O_5NAg_2$, and *potassium hydrogen*, $C_{10}H_8O_5NK$, salts are described. The *dimethyl* ester has m. p. 167°; the 4-methyl hydrogen ester, m. p. 163°, or after a year, 196—199°. Another preparation of the monomethyl ester had m. p. 208°.

Acetylmethylaminoterephthalic acid has m. p. 255° (decomp.)

The action of methyl iodide on silver hemipinate leads to the formation of the dimethyl and *a*-methyl hydrogen esters. G. Y.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XVII. Aminoterephthalic Esters. RUDOLF WEGSCHEIDER (*Monatsh.*, 1907, **28**, 819—824).—As only one of the two possible monomethyl esters of aminoterephthalic acid can be prepared directly (compare preceding abstract), the author has prepared both isomerides by reduction of the corresponding methyl hydrogen nitroterephthalates by means of tin and hydrochloric acid. The product obtained from *β*-methyl hydrogen nitroterephthalate is identical with the ester already described, and when pure has m. p. 216—217° (corr.).

1-*Methyl* 4-*hydrogen* 2-*aminoterephthalate*, obtained from *a*-methyl hydrogen nitroterephthalate, forms yellow crystals, m. p. 216—217° (corr.), and has a violet-blue fluorescence in solution. A mixture of this with the monomethyl ester, formed by esterification of aminoterephthalic acid, has m. p. 192—199°. G. Y.

Sodium Hyposulphite as a Reducing Agent for Organic Substances. EUGÈNE GRANDMOUGIN (*J. pr. Chem.*, 1907, [ii], **76**, 124—142).—An account of the author's work on the reduction of organic substances by means of sodium hyposulphite. Part of the work has been published previously (Abstr., 1906, i, 716, 967; this vol., i, 166); the following details are new.

The reaction takes place most easily when the substance to be reduced is soluble in aqueous alkalis; *p*-hydroxyazobenzene is readily reduced to aniline and *p*-aminophenol.

1-Amino-β-naphthol-3 : 6-disulphonic acid, formed by reduction of Ponceau 2R, is more stable, and reduces silver nitrate more slowly than the product obtained on reduction with stannous chloride (Witt, Abstr., 1889, 273). The following substances are obtained on reduction in the same manner of the dyes named: aniline and 1-amino-β-naphthol-3 : 6-disulphonic acid from Ponceau 2G; aniline and 1-amino-β-naphthol-6 : 8-disulphonic acid from Orange G; α-naphthylamine and 1-amino-β-naphthol-6 : 8-disulphonic acid from Crystal Ponceau; naphthionic acid and 1-amino-β-naphthol-3 : 6-disulphonic acid from Bordeaux S; naphthionic acid and 2-amino-α-naphthol-4-sulphonic acid from Azo Rubin; aniline and 2-amino-α-naphthol-4-sulphonic acid from anilineazo-α-naphthol-4-sulphonic acid.

Acetylated azo-compounds may be hydrolysed during the reduction; thus the acetyl derivatives of benzeneazo-α-naphthol and benzeneazo-β-naphthol yield 2-amino-α- and 1-amino-β-naphthols, and not the corresponding acetoxy-compounds.

Whilst azobenzene is reduced almost quantitatively to hydrazobenzene, *p*-ethoxyazobenzene yields a mixture of the hydrazo-compound with aniline and *p*-phenetidine.

o-Nitrobenzeneazosalicylic acid is reduced to hydroxyphenylbenzotriazolecarboxylic acid.

p-Nitrophenol is reduced readily in alkaline solution, forming *p*-aminophenol.

o-Nitroazobenzene is reduced to aniline, *o*-phenylenediamine, benzeneazoiminobenzene, and benzeneazoiminobenzene oxide.

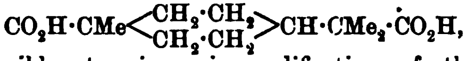
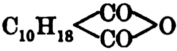
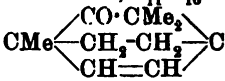
Reduction of nitroso-β-naphthol in alkaline solution leads to the formation of 1-amino-β-naphthol-4-sulphonic acid (compare Böniger, Abstr., 1894, i, 199).

Tetramethyldiaminobenzophenone is not reduced by sodium hyposulphite.

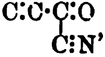
Quinizarin is reduced in alcoholic or alkaline solution, forming dihydroquinizarin, which must be 1 : 4-dihydroxyoxanthranol. When heated with aniline and glacial acetic acid, this forms a *monoanilide*, $C_{20}H_{13}O_3N$, which crystallises in dark violet needles, m. p. 153°, gives with concentrated sulphuric acid a green coloration becoming blue on addition of boric acid, and dissolves sparingly in hot alkalis or alcohol, more readily in chloroform or glacial acetic acid, forming violet to blue solutions. The *dianilide*, $C_{26}H_{18}O_2N_2$, formed by heating dihydroquinizarin with aniline, boric acid, and glacial acetic acid at 120—125°, separates in dark, glistening crystals, m. p. 218°, is dichroic in concentrated sulphuric acid solution, and forms blue solutions in alcohol, chloroform, and glacial acetic acid. Both anilides form dyes on sulphonation; that from the monoanilide dyes wool in an acid bath a bluish-violet. The dye from the dianilide dyes wool bluish-green.

Reduction of alizarin with sodium hyposulphite leads to the formation of a *product* which is not identical with Römer's deoxyalizarin (Abstr., 1881, 823), and may be 1 : 2-dihydroxyoxanthranol.

Indigotin is reduced readily by sodium hyposulphite in hot alcoholic solution, forming indigo-white. G. Y.

Menthane-1 : 8-dicarboxylic Acid and a New Dicyclic Ketone. PHILLIPE BARBIER and VICTOR GRIGNARD (*Compt. rend.*, 1907, **145**, 255—257).—By the action of magnesium on an ethereal solution of dipentene dihydrochloride, a mixture of two monomagnesium and one dimagnesium compounds is obtained together with a small quantity of dipentene. When the mixture of organomagnesium compounds is submitted to the action of carbon dioxide, two unsaturated monobasic acids, and *menthane*-1 : 8-*dicarboxylic acid*,  $CO_2H\cdot CMe{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}CH\cdot CMe_2\cdot CO_2H$, are formed. The two possible stereoisomeric modifications of the latter acid have both been isolated. The *cis*-form is a microcrystalline powder, m. p. 192°, the *cis-trans*-form, m. p. 174—175°, is more soluble in water. The former when boiled with acetic anhydride gives the *anhydride*,  $C_{10}H_{18}{<}{\substack{CO\\ CO}}{>}O$, m. p. about 145—148°, which on distillation at atmospheric pressure (compare Blanc, this vol., i, 220) evolves carbon dioxide and hydrogen, and forms the ketone, $C_{11}H_{16}O$. For the latter, the authors propose the formula  $CMe{\substack{CO\cdot CMe_2\\ CH_2{-}CH_2\\ CH{=}CH}}CH$, and assign to it the name 1 : 3 : 3-*trimethyl* 1 : 7 : 8 : 4-*di*cyclo-Δ^5-*hexene*-2-*one*. It forms a greenish-yellow liquid, b. p. 93—95°/13 mm., D^0 0·9886, n_D 1·49018.

E. H.

Reaction of Organic Magnesium Compounds with Cinnamylidene Esters. I. Reactions with Methyl Cinnamylidenemalonate. MARIE REIMER (*Amer. Chem. J.*, 1907, **38**, 227—237).—Experiments on the behaviour of Grignard's reagent towards α-cyanocinnamylideneacetic acid showed that the reaction was much more complex than in the case of α-cyanocinnamic acid (Kohler and Reimer, Abstr., 1905, i, 347). Since both these compounds contain the system,  $C{:}C\cdot\underset{C{:}N}{C}{:}O$, it seemed likely that the complexity of the reaction was due to the influence of the additional double linking in the system, $C{:}C\cdot C{:}C\cdot C{:}O$, rather than to the presence of the cyano-group, although Kohler (Abstr., 1906, i, 427) has shown that this group does react with Grignard's reagent. The object of the investigation, now being carried out, is to study the effect of the double linking on the reactivity of the system $C{:}C\cdot C{:}O$. The results described in the present paper show that the compounds produced by the action of both aromatic and aliphatic magnesium compounds on methyl cinnamylidenemalonate are formed by 1 : 4-addition.

Methyl β-phenyl-γ-benzylidene-ethylmalonate,

$$CHPh{:}CH\cdot CHPh\cdot CH(CO_2Me)_2,$$

m. p. 94°, obtained by the action of magnesium phenyl bromide on methyl cinnamylidenemalonate, crystallises in white prisms. *β-Phenyl-γ-benzylidene-ethylmalonic acid*, m. p. 166° (decomp.), separates from hot water in slender, white needles. On heating this acid at 175°, it is converted into *β-phenyl-γ-benzylidenebutyric acid*,

$$CHPh{:}CH\cdot CHPh\cdot CH_2\cdot CO_2H,$$

m. p. 118°, which forms long, slender needles.

By the action of magnesium methyl iodide on the ester, *methyl γ-benzylidene-β-methylethylmalonate*, b. p. 210°/30 mm., is produced. The *acid*, $CHPh{:}CH\cdot CHMe\cdot CH(CO_2H)_2$, m. p. 120—121°, crystallises in small, white needles, and, when heated at 160°, is converted into *γ-benzylidene-β-methylbutyric acid*, $CHPh{:}CH\cdot CHMe\cdot CH_2\cdot CO_2H$, m. p. 51—52°, which forms hard needles.

Magnesium benzyl chloride reacts with the ester with formation of an *acid*, probably $CHPh{:}CH\cdot CH(CH_2Ph)\cdot CH(CO_2H)_2$, which crystallises in white needles. On heating this acid at 180° and oxidising the product, benzoic and benzylsuccinic acids are obtained, whence it is evident that the decomposition takes place thus:

$$CHPh{:}CH\cdot CH(CH_2Ph)\cdot CH(CO_2H)_2 \longrightarrow$$
$$CHPh{:}CH\cdot CH(CH_2Ph)\cdot CH_2\cdot CO_2H \longrightarrow$$
$$C_6H_5\cdot CO_2H + CO_2H\cdot CH(CH_2Ph)\cdot CH_2\cdot CO_2H.$$

E. G.

Action of Methylamine on Salicylic Acid and Methyl *o*-Ethoxybenzoate. FRANCESCO NICOLA (*Chem. Zentr.*, 1907, ii, 49—50; from *Giorn. Farm Chim.*, 1907, 56, 193—197).—A 33% solution of methylamine acts on methyl salicylate in the same way as ammonia, but only yields salicylmethylamide after heating at 100° for four hours. Methyl *o*-ethoxybenzoate is hydrolysed forming *o*-ethoxybenzoic acid. *Salicylmethylamide*, $OH\cdot C_6H_4\cdot CO\cdot NHMe$, m. p. 91°, forms white leaflets and is very readily soluble in alcohol or ether, rather soluble in boiling water, but very sparingly so in cold water. When ferric chloride is added to the aqueous solution, a violet coloration is formed, and by the action of potassium hydroxide, methylamine and potassium salicylate are obtained.

E. W. W.

Observations on Aldehydes. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 199—204).—The author has examined certain aldehydes to ascertain whether they are in accord with the classification of aldehydes into: (I.) true aldehydes, which give all the reactions of aldehydes, including those of Angeli and Marchetti (this vol., i, 551), and Doebner (Abstr., 1894, i, 261, 532), and are comparable with true nitroso-derivatives. (II.) Aldehydes, which are not sugars, which give all the reactions of aldehydes with the exception of that of Angeli and Marchetti, and are analogous to *iso*nitroso-derivatives and are hence termed *iso*aldehydes. (III.) The aldoses, which give neither Angeli and Marchetti's reaction nor that of Doebner and are called pseudo-aldehydes.

Pyrrole-2-aldehyde, when heated with pyruvic acid and β-naphthylamine in absolute alcoholic solution, yields *2-pyrryl-2-naphthacinchonic acid*, $C_{18}H_{12}O_2N_2$, which is a yellow substance, m. p. 300° (decomp.).

Similarly, *o*-nitrobenzaldehyde yields *2-o-nitrophenylnaphthacinchonic acid*, $C_{20}H_{12}O_4N_2$, which crystallises from alcohol in microscopic needles, m. p. 265° (decomp.), and glycollaldehyde gives *2-methoxynaphthacinchonic acid*, $C_{15}H_{11}O_3N$, which separates from alcohol in crystals, m. p. 255°.

Glycollaldehyde also gives Angeli and Marchetti's reaction.

T. H. P.

Spontaneous Oxidation in Presence of Hydramides. MARIO BETTI (*Gazzetta*, 1907, **37**, ii, 91—99).—The oxidation of 1-phenyl-3-methyl-5-pyrazolone in alcoholic ammonia solution to rubazonic acid (Abstr., 1906, i, 985) takes place when the benzaldehyde is replaced by another aromatic aldehyde. With salicylaldehyde, the rubazonic acid is accompanied by 4-salicylidene-bis-1-phenyl-3-methyl-5-pyrazolone; with anisaldehyde, by 4-anisylidene-bis-1-phenyl-3-methyl-5-pyrazolone, and so on; the hydramide derivatives formed by these aldehydes with ammonia accelerate the oxidation more than the aldehydes themselves. The oxidation also occurs in presence of formaldehyde, but not with other aliphatic aldehydes or acetone; formaldehyde has a strong tendency to react with ammonia, yielding hexamethylenetetramine, a compound which, in some ways, is analogous to the aromatic hydramides.

The conclusion is drawn that the oxidation is not effected by those aldehydes having the characteristic property of giving, with ammonia, additive products of the type $R{\cdot}CH(OH){\cdot}NH_2$, in the formation of which no oxygen becomes detached. On the other hand, aldehydes which react with ammonia, forming compounds of the type $R{\cdot}CH{:}NX$, and liberating oxygen in the form of water, act energetically in bringing about the oxidation. The action may, indeed, be a catalytic one, depending on this detachment of oxygen from the aldehyde molecule.

In anhydrous solutions, the reaction proceeds very slowly at first, but rapidly after an hour or so. The presence of a small quantity of water hence appears to exert an influence on the reaction. The oxidation is, however, not affected by the bis-pyrazolone compounds formed with the rubazonic acid. T. H. P.

Intramolecular Atomic Transpositions. VII. Influence of Substituents of the Phenyl Group on the Transformation of Benzopinacones into Benzopinacolins. P. J. MONTAGNE (*Rec. trav. chim.*, 1907, **26**, 253—272. Compare this vol., i, 140, 141).—When treated with acetyl chloride, benzopinacone and its derivatives are converted into benzopinacolins, the transformation being accompanied by the migration of a phenyl group. When, however, not only phenyl groups but also substituted phenyl groups are attached to the $\dot{\colon}C(OH){\cdot}C(OH)\dot{\colon}$ residue, migration of either of these two kinds of groups may occur. The author proposes to examine this migration for pinacones containing differently substituted phenyl radicles, so as to ascertain, in each case, whether these radicles migrate more easily or more difficultly than phenyl itself. Thörner and Zincke (Abstr., 1878, i, 223) have shown that, when heated with acetyl chloride, *s*-diphenyldi-*p*-tolylpinacone is converted into β-di-*p*-tolyldiphenylpinacolin, and Acree (Abstr., 1905, i, 216) states that this transformation is quantitative. *p*-Tolyl hence migrates more readily than phenyl. In the case of *s*-diphenyldi-*p*-chlorophenylpinacone, the author finds that both the phenyl and *p*-chlorophenyl radicles migrate, but the former (60%) to a greater extent than the latter (40%). The influence of the chlorine atom on the migration of phenyl is hence opposed to, and weaker than, that exerted by the methyl group. This result is not in accord with the general law laid down by Tiffeneau (Abstr., 1902, i, 666) to the effect that the tendency of the phenyl group to migrate according to the scheme $\cdot CPh\colon CH_2 \longrightarrow R\cdot CO\cdot CH_2Ph$ is greatly enhanced when the phenylic hydrogen is replaced by substituents which increase its molecular magnitude and hence also its ability to migrate.

s-*Diphenyldi* p-*chlorophenylpinacone*,

$$C_6H_4Cl\cdot CPh(OH)\cdot CPh(OH)\cdot C_6H_4Cl,$$

prepared by reducing *p*-chlorobenzophenone either by the action of sunlight on its alcoholic solution or by means of zinc dust and acetic acid, separates from alcohol in white crystals, m. p. 168° (decomp.).

p-*Chlorobenzhydrol*, $C_6H_4Cl\cdot CHPh\cdot OH$, prepared by reducing *p*-chlorobenzophenone either by zinc dust and acetic acid or by sodium amalgam and alcohol, crystallises from light petroleum in long needles, m. p. 62°, and has the normal molecular weight in boiling benzene.

4-*Chlorodiphenylmethane*, $CH_2Ph\cdot C_6H_4Cl$, prepared by reducing *p*-chlorobenzophenone by means of phosphorus and hydriodic acid in acetic acid solution, has b. p. 298°/742·5 mm., and has the normal molecular weight in boiling benzene. T. H. P.

Intramolecular Atomic Transpositions. VIII. Preparation of 2:4:6-Trichlorobenzophenone and of Phenyl *α*- and *β*-Naphthyl Ketones. P. J. MONTAGNE (*Rec. trav. chim.*, 1907, **26**, 273—284).—2 : 4 : 6-*Trichlorobenzophenone*, $C_6H_2Cl_3\cdot COPh$, prepared by the interaction of benzoyl chloride and 1 : 3 : 5-trichlorobenzene in presence of aluminium chloride, separates from light petroleum in shining, prismatic crystals belonging to the triclinic system [F. M. JAEGER, $a:b:c = 1\cdot3908:1:1\cdot1537$; $\alpha = 129°56\frac{3}{4}'$, $\beta = 123°21\frac{2}{3}'$, $\gamma = 60°26'$], m. p. 103·5°, b. p. 356°/763 mm.

2 : 4 : 6-Trichlorobenzamide, already prepared (Abstr., 1903, i, 169), separates from a mixture of absolute alcohol, light petroleum, and benzene in shining, rhombic crystals [F. M. JAEGER, $a:b:c = 0\cdot5380:1:1\cdot5180$].

The interaction of benzoyl chloride and naphthalene in carbon disulphide solution in presence of aluminium chloride yields a mixture of phenyl *α*-naphthyl ketone (78·5%), m. p. 75·5°, b. p. 386°/764 mm. or 225°/12 mm., and phenyl *β*-naphthyl ketone (14%), m. p. 82°, b. p. 398°/754 mm., which were separated by crystallising from alcohol, the *α*-derivative being deposited first. T. H. P.

2 : 4 : 2′ : 4′-Tetramethylbenzophenone. JACOB BÖESEKEN (*Rec. trav. chim.*, 1907, **26**, 285—288).—The tetramethylbenzophenone, obtained by the interaction of *m*-xylene and an excess of carbon tetrachloride in presence of aluminium chloride (Abstr., 1905, i, 423), does not yield an oxime or a hydrazone. It is, however, found to be identical with the ketone obtained by distillation of calcium 2 : 4-dimethylbenzoate, and is hence 2 : 4 : 2′ : 4′-tetramethylbenzophenone, $C_6H_3Me_2\cdot CO\cdot C_6H_3Me_2$. The constants for the compound are: (1) prepared from *m*-xylene and carbon tetrachloride, b. p. 185°/5 mm., D^{12} 1·0506, D^{15} 1·0477, n_D^{12} 1·5876; (2) prepared from calcium 2 : 4-dimethylbenzoate, b. p. 188°/7 mm., D^{15} 1·043, n_D^{15} 1·5869.

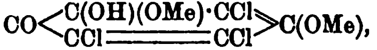
When the ketone is boiled with zinc in a faintly alkaline alcoholic solution, no reduction takes place, only 2 : 4-dimethylbenzoic acid being formed. T. H. P.

Some Derivatives of Tetrachloro-*o*-benzoquinone. C. Loring Jackson and Robert D. MacLaurin (*Amer. Chem. J.*, 1907, **38**, 127—175. Compare Abstr., 1906, i, 97).—Jackson and Porter (Abstr., 1903, i, 266 ; 1904, i, 254) have shown that by the action of methyl alcohol on tetrabromo-*o*-benzoquinone, two substances are formed, namely, the compound $4C_6O_2Br_4,MeOH$ and the *a*-compound (octabromo-1′-hydroxy-1-methoxy-*o*-benzoquino-1-monoxide). By the action of various reagents on the *a*-compound, the isomeric *β*-compound (octabromo-1′-hydroxy-1-methoxy-*o*-benzoquino-1 : 2 : 2-trioxide) is produced. Further work on these substances has been carried out by Jackson and Carlton (Abstr., 1905, i, 907), Jackson and Russe (Abstr., 1906, i, 288), and by Jackson and MacLaurin (this vol., i, 223).

The action of methyl alcohol on tetrachloro-*o*-benzoquinone has now been studied and the following six products have been isolated. The *β*-compound (octachloro-1′-hydroxy-1-methoxy-*o*-benzoquino-1 : 2 : 2-trioxide), 3 : 5 : 6-trichloro-4-methoxy-*o*-benzoquinone methylhemiacetal, 3 : 5 : 6-trichloro-2-hydroxy-*p*-benzoquinone, chloroanilic acid, hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether, and hexachloro-*o*-benzoquinodimethylhemiacetalcatechol ether. The difference in the products obtained from the tetrabromo- and tetrachloro-*o*-quinones is chiefly ascribed to the fact that in the former compound the action is confined to the oxygen atoms, whilst in the latter compound the chlorine also takes part in the reaction.

The *β-compound* (*octachloro-*1′-*hydroxy-*1-*methoxy-o-benzoquino-*1 : 2 : 2-*trioxide*), $\mathrm{OMe{\cdot}C_6Cl_4{:}O_3{:}C_6Cl_4{\cdot}OH}$, m. p. 157°, forms rhombic plates, and has a structure corresponding with that of the *β*-compound obtained from tetrabromo-*o*-quinone (this vol., i, 223).

3 : 5 : 6-*Trichloro-*4-*methoxy-o-benzoquinone methylhemiacetal*,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{C(OH)(OMe){\cdot}CCl}\\ \mathrm{CCl{=\!=\!=}CCl}\end{matrix}{>}\mathrm{C(OMe)},$$

m. p. 138—140°, crystallises in thick, white, rhombic plates ; its *acetyl* derivative has m. p. 149—150°, and its *phenylhydrazone*, m. p. 235°. By the action of concentrated hydrochloric acid on this compound, it is converted into 3 : 5 : 6-trichloro-2-hydroxy-*p*-benzoquinone (Zincke and Schaum, Abstr., 1894, i, 233).

Hexachloro-o-benzoquinomethylhemiacetalcatechol ether,

$$\mathrm{C_6Cl_4O_2{:}C_6Cl_2O(OH)(OMe)},$$

m. p. 198°, crystallises in yellow needles and yields an *acetyl* derivative, m. p. 215°. The *diacetyl* derivative of hexachlorodihydroxycatechol ether, m. p. 290°, forms white, lustrous leaflets.

Hexachloro-o-benzoquinodimethylhemiacetalcatechol ether,

$$\mathrm{C_6Cl_4O_2{:}C_6Cl_2(OH)_2(OMe)_2},$$

m. p. 218°, crystallises in white plates, and when gently heated with strong sulphuric acid is converted into hexachloro-*o*-benzoquinocatechol ether, whilst on reduction or by the action of hydrochloric acid it is converted into hexachlorodihydroxycatechol ether.

The remarkable observation was made during the course of these experiments that when 3 : 5 : 6-trichloro-2-hydroxy-*p*-benzoquinone is left with methyl alcohol and hydrochloric acid, hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether is produced, a *p*-quinone thus being converted into a derivative of an *o*-quinone.

By the action of ethyl alcohol on tetrachloro-*o*-benzoquinone, four compounds are formed, namely, 3 : 5 : 6-trichloro-2-hydroxy-*p*-benzoquinone, chloroanilic acid, a *compound*, m. p. 115°, and, as principal product, a *compound*, $C_{28}H_{12}O_{10}Cl_{12}$, m. p. 210°, which forms yellow, rhombic plates and probably consists of hexachloro-*o*-benzoquinocatechol ether (2 mols.) combined with ethyl alcohol (2 mols.).

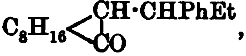
n-Propyl and *iso*amyl alcohols react with tetrachloro-*o*-benzoquinone with formation of 3 : 5 : 6-trichloro-2-hydroxy-*p*-benzoquinone and chloroanilic acid. *iso*Propyl alcohol yields only chloroanilic acid, whilst *tert.*-butyl alcohol furnishes a product, m. p. 250°, which may be the *β-compound, octachloro-*1-tert.-*butyloxy-*1′-*hydroxy-o-benzoquino-*1 : 2 : 2-*trioxide.* Benzyl alcohol gives a yellow *substance*, m. p. 215°.

When tetrachloro-*o*-benzoquinone is treated with ordinary undried toluene, the following four products are obtained. Tetrachloro-*o*-benzoquinone with 1 mol. toluene of crystallisation; the *a*-water *compound*, $OH{\cdot}C_6Cl_4{\cdot}O_2{\cdot}C_6Cl_4{\cdot}OH$, m. p. 172°, which crystallises in needles; a small quantity of a brown *compound*, m. p. 182—183°; and a *substance*, $C_{24}HO_8Cl_{18}$, m. p. 290°, which is probably composed of the hexachloro-*o*-benzoquinocatechol ether (1 mol.) with heptachloro-*o*-benzoquinocatechol hemiether (1 mol.), but the way in which these ethers are united in the substance has not yet been ascertained.

By the action of glacial acetic acid on tetrachloro-*o*-benzoquinone, the *a-compound, octachloro-*1-*acetoxy-*1′-*hydroxy-o-benzoquino-*1-*monoxide*, $OAc{\cdot}C_6Cl_4{:}O_3{:}C_6Cl_4{\cdot}OH$, m. p. 250—252°, is produced, which crystallises in white needles.

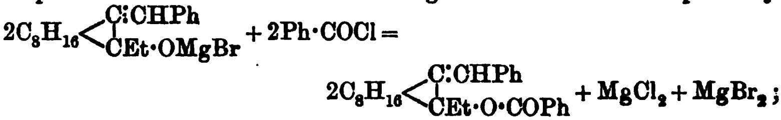
When tetrachloro-*o*-benzoquinone is warmed with water for a few minutes, it is converted into hexachloro-*o*-benzoquinocatechol ether. If this ether is treated with methyl alcohol, it yields hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether, whilst if a little water is added to the methyl alcohol, hexachloro-*o*-benzoquinodimethylhemiacetalcatechol ether and chloroanilic acid are produced. Ethyl alcohol reacts with the ether with formation of chloroanilic acid and a compound, m. p. 210°, identical with that obtained by the action of ethyl alcohol on tetrachloro-*o*-benzoquinone. *n*-Propyl alcohol yields a *compound*, m. p. 210°. Phenylhydrazine reduces the ether to hexachlorodihydroxycatechol ether. E. G.

Derivatives of Menthone. EYVIND BÖDTKER (*Compt. rend.*, 1907, **145**, 329—331).—Organo-magnesium compounds do not act on ethylmenthone (compare Haller and Bauer, Abstr., 1906, i, 440, 441). When an ethereal solution of benzylidenementhone is added to a solution of magnesium ethyl bromide, *phenylmenthylethylmethane*,

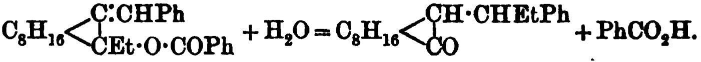


$$C_8H_{16}\langle\begin{matrix}CH{\cdot}CHPhEt\\ |\\ CO\end{matrix}$$

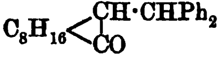
, which forms white needles, m. p. 102·5—103·5°, $[a]_D$ −79°34′, in benzene solution, and a *substance* crystallising in fine needles in quantity insufficient for analysis, m. p. 83—84°, are formed. If before treating with water, benzoyl chloride (1 mol.) is added to the reaction-product a further reaction occurs and the viscous substance obtained, after saponification with alcoholic potash, gives white needles, m. p. 102·5—103·5°, identical with the above, and a stereoisomeride, m. p. 89—91°. The reactions occurring in the latter case are probably



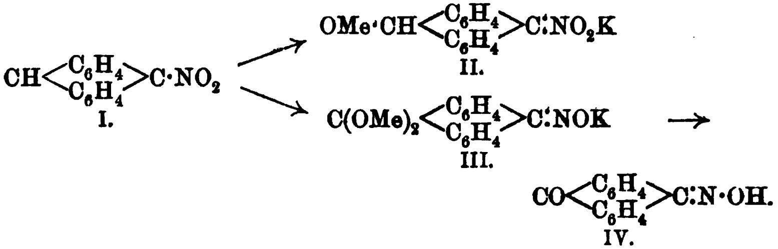
$$2C_8H_{16}<\begin{matrix}\text{C:CHPh}\\ \text{CEt·OMgBr}\end{matrix} + 2\text{Ph·COCl} = 2C_8H_{16}<\begin{matrix}\text{C:CHPh}\\ \text{CEt·O·COPh}\end{matrix} + MgCl_2 + MgBr_2;$$



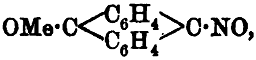
$$C_8H_{16}<\begin{matrix}\text{C:CHPh}\\ \text{CEt·O·COPh}\end{matrix} + H_2O = C_8H_{16}<\begin{matrix}\text{CH·CHEtPh}\\ \text{CO}\end{matrix} + PhCO_2H.$$

If bromobenzene is used instead of ethyl bromide, the product consists of *diphenylmenthylmethane*,  $C_8H_{16}<\begin{matrix}\text{CH·CHPh}_2\\ \text{CO}\end{matrix}$, slender needles, m. p. 139—140°, feebly dextrorotatory in benzene solution. By means of the benzoyl chloride reaction, two stereoisomerides are obtained, one having m. p. 160·5—161·5°, $[\alpha]_D$ −158°30′, the other m. p. 136—137°, and inactive. A mixture of the latter with the substance, m. p. 139—140°, has m. p. 130°, whilst alcoholic potash transforms the substance, m. p. 139—140°, into its isomeride, m. p. 136—137°. E. H.

Reactions of Unsaturated Nitro-compounds. Jakob Meisenheimer (*Annalen*, 1907, 355, 249—311).—The transformation of 9-nitroanthracene into the isomeric anthraquinoneoxime has already been interpreted by the author (Abstr., 1902, i, 795), thus:



$$\underset{\text{I.}}{CH<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C\cdot NO_2} \begin{matrix}\nearrow \underset{\text{II.}}{OMe\cdot CH<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C:NO_2K}\\ \searrow \underset{\text{III.}}{C(OMe)_2<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C:NOK} \rightarrow \end{matrix} \underset{\text{IV.}}{CO<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C:N\cdot OH.}$$

(I) is converted into (II) by 5% cold methyl-alcoholic potassium hydroxide and into (III) by 10% boiling methyl-alcoholic potassium hydroxide; (II) is converted into (III) by 10% boiling methyl-alcoholic potassium hydroxide, and (III) into (IV) by dilute mineral acids. The mechanism of those changes was clear, with the exception of the change of (II) into (III) and, with the object of elucidating this particular phase, the work recorded in the present paper was undertaken. Evidence is submitted for the formation of nitrosomethoxyanthracene,  $OMe\cdot C<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>C\cdot NO$, as intermediate between (II) and (III).

A large number of nitro-compounds has been investigated from the same standpoints.

[With Friedrich Heim.]—The action of alkalis on phenylnitroethylene has already been studied by Meisenheimer and Heim (Abstr., 1905, i, 269). Phenylnitroethylene interacts with sodium methoxide in methyl-alcoholic solution, thus:

$$CHPh{:}CH{\cdot}NO_2 + NaOMe = OMe{\cdot}CHPh{\cdot}CH{:}NO_2Na.$$

The resulting solution quickly changes with production of resins. With dilute methoxide at the ordinary temperature, from 20—30% of βδ-dinitro-α-methoxy-αγ-diphenylbutane,

$$OMe{\cdot}CHPh{\cdot}CH(NO_2){\cdot}CHPh{\cdot}CH_2{\cdot}NO_2$$

(*loc. cit.*), was isolated together with appreciable amounts of the corresponding benzoic ester, the bulk of the nitroethylene resinifying. Accordingly, 2 mols. of nitroethylene react with 1 mol. of alcohol, and the acetaloxime anticipated was not formed.

The molecular weight of βδ-dinitro-α-methoxy-αγ-diphenylbutane was determined in ethylene dibromide solution. Further details regarding the sodium salt and the tribromo-derivative,

$$OMe{\cdot}CHPh{\cdot}CBr(NO_2){\cdot}CHPh{\cdot}CBr_2{\cdot}NO_2,$$

are given. The *dibromo*-derivative, $C_{17}H_{16}O_5N_2Br_2$, obtained as a by-product in the preparation of the tribromo-derivative, separates from acetone in prisms, m. p. 186° (decomp.). Another *bromide*, $C_9H_9O_3NBr_2$, obtained by the action of bromine (4 atoms) on the sodium salt, crystallises from methyl alcohol in glistening leaflets, m. p. 156°.

The behaviour of βδ-dinitro-α-methoxy-αγ-diphenylbutane towards concentrated methyl-alcoholic potassium hydroxide was studied. The acetaloxime anticipated was, however, not obtained, disruption taking place with the formation of benzoic acid and a brown resin. It is supposed that the acetaloxime is not stable under the conditions employed.

Phenylnitroethylene is converted by exposure to light into a compound, which is not *iso*phenylnitroethylene, as Priebs supposes, but is the *polymeride*, $(C_8H_7O_2N)_2$; it dissolves in alkalis, but is reprecipitated by acids.

Better results were obtained by the authors with α-nitrostilbene. This compound may be prepared according to Knoevenagel and Walter (Abstr., 1905, i, 65) by the condensation of phenylnitromethane with benzaldehyde by aid of aliphatic bases or by the action of alkali on either the α- or the β-form of diphenyldinitroethane, thus:

$$NO_2{\cdot}CHPh{\cdot}CHPh{\cdot}NO_2 - HNO_2 \longrightarrow CHPh{:}CPh{\cdot}NO_2;$$

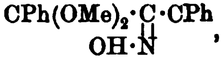
the same compound is formed, no matter whether the α- or β-form referred to is used, although two α-nitrostilbenes are theoretically possible.

α-Nitrostilbene readily acts on sodium methoxide to form β-nitro-α-methoxy-αβ-diphenylethane, which, by the action of concentrated methyl-alcoholic potassium hydroxide, gives the anticipated acetal.

The stilbene, necessary for the preparation of the diphenyldinitroethanes, was prepared from benzyl chloride by means of Grignard's reaction, but the method, although the best of those attempted, does not give a satisfactory yield. *β-Nitro-α-methoxy-αβ-diphenylethane*(α), $OMe{\cdot}CHPh{\cdot}CHPh{\cdot}NO_2$, obtained by the addition of sodium methoxide to (α)-diphenyldinitroethane dissolved in methyl alcohol, separates from methyl alcohol in colourless needles, m. p. 130—131°. It is not changed when boiled for half an hour with 28% methyl-alcoholic potassium hydroxide. The corresponding *β-nitro-α-methoxy-αβ-diphenylethane*(β) crystallises in prisms, m. p. 97—98°; when carbon dioxide is passed into its alkaline solution, the α-form is precipitated.

7-Nitrostilbene is readily obtained from either form. *β-Nitro-α-ethoxy-αβ-diphenylethane*, $C_{16}H_{17}O_3N$, obtained from α-nitrostilbene and ethyl-alcoholic potassium hydroxide, forms colourless needles, m. p. 92°.

syn.-*Benzilmonoximedimethylacetal*,



$$\begin{array}{l}\mathrm{CPh(OMe)_2{\cdot}C{\cdot}CPh}\\ \qquad\quad\ \ \mathrm{OH{\cdot}\overset{\|}{N}}\end{array}$$

, obtained by the action of 28% methyl-alcoholic potassium hydroxide on nitromethoxydiphenylethane at 150°, forms silky needles, m. p. 208° (decomp.). Its *benzyl ether*, $C_{23}H_{23}O_3N$, crystallises from methyl alcohol in colourless prisms, m. p. 71—72°, and is converted by concentrated hydrochloric acid into α-benzilmonoxime benzyl ether, m. p. 94—95°. *syn.*-Benziloximedimethylacetal was also defined by its direct conversion into β-benzilmonoxime by means of concentrated hydrochloric acid.

[With Leo Jochelson.]—The behaviour of α-nitro-4′-methoxy-stilbene towards alkali is similar to that of α-nitrostilbene itself. In methyl-alcoholic solution, it combines with alkali methoxides very readily with the formation of β-nitro-α-methoxy-α-anisyl-β-phenylethane. The latter compound is very stable towards alkali in methyl-alcoholic solution, but at 160—170° is converted into 4′-methoxybenzilmonoxime-ββ-dimethylacetal, which is saponified by cold concentrated hydrochloric acid with the formation of 4′-methoxybenzilmonoxime. The following phases may thus be realised:

$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}NO_2 \longrightarrow OMe{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CPh{:}NO_2K \longrightarrow}$
$\mathrm{OMe{\cdot}C_6H_4{\cdot}C(OMe)_2{\cdot}CPh{:}N{\cdot}OH \longrightarrow OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CPh{:}N{\cdot}OH}$.

These reactions proceed quantitatively with the exception of the formation of the acetaloxime.

α-Nitro-4′-methoxystilbene was prepared by the condensation of phenylnitromethane with anisaldehyde.

β-Nitro-α-methoxy-α-anisyl-β-phenylethane,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH(OMe)CHPh{\cdot}NO_2},$$

crystallises from methyl alcohol in silky needles, m. p. 139°.

4′-*Methoxybenzilmonoxime-ββ-dimethylacetal*,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}C(OMe)_2{\cdot}CPh{:}N{\cdot}OH},$$

separates from methyl alcohol in colourless needles, m. p. 206—208° (decomp.). Its solution in concentrated sulphuric acid is blood-red, and when poured into water it yields anisic acid. As by-products in its preparation, anisic acid, benzoic acid, benzaldehyde, and benzaldoxime (in an impure state) were isolated.

Methoxybenziloximedimethylacetal methyl ether,

$$\mathrm{OMe{\cdot}C_6H_4{\cdot}C(OMe)_2{\cdot}CPh{:}N{\cdot}OMe},$$

obtained by the action of methyl iodide on a solution of the acetaloxime in a mixture of methyl alcohol and concentrated methyl-alcoholic potassium hydroxide, crystallises from methyl alcohol in colourless needles, m. p. 82—83°.

4′-*Methoxybenziloxime*, $\mathrm{OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CPh{:}N{\cdot}OH}$, crystallises from methyl alcohol in colourless, prismatic needles, m. p. 130—131°. Its solution in concentrated alkali is yellow. Its *methyl ether* separates from methyl alcohol in colourless crystals, m. p. 93—94°; sometimes a *stereoisomeride* is formed, which crystallises from methyl alcohol in glistening, silvery needles, m. p. 79·5°, and is the less stable of the two forms; it is not decided which modification is *syn*- and which *anti*-.

p-Methoxydeoxybenzoin (4′-methoxy-β-ketodibenzyl),

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph,$$

obtained by the reduction of 4′-methoxybenziloxime, or of the acetaldoxime with zinc dust and acetic acid, crystallises from methyl alcohol in colourless, stellate needles, m. p. 77—78°. The formation from the benziloxime is probably accompanied by the transient existence of an oxyethylamine, thus:

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CPh{:}N{\cdot}OH \longrightarrow OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHPh{\cdot}NH_2 \longrightarrow$$
$$OMe{\cdot}C_6H_4{\cdot}C(OH){:}CHPh \longrightarrow OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph.$$

When acted on by bromine, the preceding deoxybenzoin forms p *methoxybromodeoxybenzoin* (*4′-methoxy-α-bromo-β-ketodibenzyl*),

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHPhBr,$$

which crystallises from methyl alcohol in colourless needles, m. p. 73—74°, and, by treatment with sodium carbonate, yields *p*-methoxybenzoin, m. p. 108°.

The next section of the work deals with the behaviour of derivatives of β-nitroanethole, which readily acts on alkali methoxide; by the action of carbon dioxide, 1-anisyl-2-nitropropane-1-oxymethane is formed.

β-Nitroanethole was prepared by the action of alcoholic ammonia on anethole*pseudo*nitrosite.

β-Nitro-α-methoxy-α-anisylpropane, $OMe{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CHMe{\cdot}NO_2$, is a yellow liquid, b. p. 172—174·5°/12—14 mm. When acted on by bromine water, it forms *β-bromo-β-nitro-α-methoxy-α-anisylpropane*, $OMe{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CBrMe{\cdot}NO_2$, which crystallises from petroleum in silvery needles, m. p. 76°.

β-Nitro-α-methoxy-α-anisylpropane is very stable towards alkali, differing in this respect from the behaviour of the methyl alcohol additive product derived from phenylnitroethylene and resembling the corresponding products from the nitrostilbenes described. After boiling for ten hours with very concentrated methyl-alcoholic potassium hydroxide, it is partly unchanged; the bulk is resinified, whilst from 10% to 20% yields anisic acid, anisaldehyde, and anisyl alcohol. The following changes doubtless take place:

$$(1)\ OMe{\cdot}C_6H_4{\cdot}CH(OMe){\cdot}CMe{:}NO_2K + H_2O =$$
$$OMe{\cdot}C_6H_4{\cdot}CHO + CHMe{:}NO_2K + MeOH;$$
$$(2)\ 2OMe{\cdot}C_6H_4{\cdot}CHO + H_2O = OMe{\cdot}C_6H_4{\cdot}CO_2H + OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH.$$

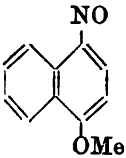
It is probable that an acetaloxime is produced as an intermediate product which undergoes decomposition in the presence of the strong alkali, thus:

$$OMe{\cdot}C_6H_4{\cdot}C(OMe)_2{\cdot}CMe{:}N{\cdot}OH + 2H_2O =$$
$$OMe{\cdot}C_6H_4{\cdot}CO_2H + CHMe{:}N{\cdot}OH + 2MeOH.$$

The author next gives the experimental details accumulated by himself with 1-nitronaphthalene and 9-nitrophenanthrene respectively. 1-Nitronaphthalene is very sensitive towards hot alcoholic alkali;

when boiled with alkali, it is converted into a black mass, which could not be crystallised, but small amounts of products which were soluble in alkali were obtained. At 22—24°, the action is slower, but it was not possible to detect in the filtrate the nitrodihydronaphthol methyl ether which might be anticipated to result from the action of potassium methoxide. The filtrate contained *4-nitroso-1-naphthol methyl ether*, $C_{11}H_9O_2N$, which crystallises from methyl alcohol in yellowish-green needles, m. p. 64—65°. When water is added to the green methyl-alcoholic solution of the preceding compound, a green oil is precipitated which, on the addition of a trace of dilute hydrochloric acid, is converted into naphthaquinoneoxime, the potassium salt of which was analysed. *1 : 4-Naphthaquinoneoxime methyl ether*, $C_{11}H_9O_2N$, obtained by the addition of methyl-alcoholic potassium hydroxide to a methyl-alcoholic solution of naphthaquinoneoxime, and subsequent addition of methyl iodide to the resulting potassium salt, separates from methyl alcohol in bright yellow needles, m. p. 80—82°.

When alkali is added to the green solution of 4-nitroso-1-naphthol methyl ether in methyl alcohol, a change of tint to yellow occurs, and this solution contains without doubt the potassium salt of 1 : 4-naphthaquinoneoxime dimethylacetal, although the salt could not be isolated.



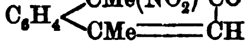
The colour of these compounds is of interest. The nitrosonaphthol ether is green in accordance with the annexed structure. The naphthaquinoneoxime, on the other hand, is faintly yellow and almost colourless, a fact which is not in accordance with a quinonoid structure, especially when one considers that the corresponding quinone is intensely yellow. The potassium salt, obtained from the naphthaquinoneoxime, is, however, dark yellowish-brown, and its solutions are reddish-brown.

The author is inclined to assign a quinonoid structure to the potassium salt, and a non-quinonoid structure to the free oxime.

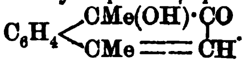
9-Nitrophenanthrene is attacked by methyl-alcoholic potassium hydroxide with comparative difficulty; there is no action in the cold, but, on heating, action takes place, although the primary product, nitrodihydrophenanthrol methyl ether, could not be isolated. When the product, obtained by boiling for ½ hour, is poured into an excess of water, a slight precipitate, probably consisting of azo- and azoxy-phenanthrene, is formed. When the aqueous solution is extracted with ether, *phenanthrenequinoneoximedimethylacetal*, $C_{16}H_{15}O_3N$, is obtained as colourless prisms, m. p. 166—167° (decomp.). The alkaline mother liquors, from which the preceding compound had been isolated, gave an appreciable amount of phenanthraquinoneoxime, m. p. 158°.

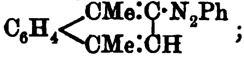
A. McK.

1 : 4-Dimethyl-2-naphthaquinol. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 205—214).—By the action of nitrous acid on 1 : 4-dimethyl-2-naphthol in ethereal solution, the author obtains the dimethylnaphthaquinonitrole,



$C_6H_4{<}\begin{array}{l}CMe(NO_2)\cdot CO\\ CMe{=\!=}CH\end{array}$

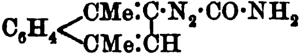
(compare Zincke, Abstr., 1903, i, 756), which is converted by the action of ether and acetic acid into the dimethylnaphtha-ψ-quinol (compare Bamberger, Abstr., 1901, i, 141),  $C_6H_4<\begin{matrix}\mathrm{CMe(OH)\cdot CO}\\ \mathrm{CMe{=\!=}CH}\end{matrix}$. This latter compound is found to be identical with the compound, m. p. 104—105°, prepared by Cannizzaro and Carnelutti (Abstr., 1883, 77; compare also Cannizzaro and Andreocci, Abstr., 1896, i, 488), and termed by them oxydimethylnaphthol. The compound described as the phenylhydrazone of the latter (Cannizzaro and Andreocci, *loc. cit.*) must, in the light of Bamberger's researches (Abstr., 1902, i, 509), be regarded as benzeneazodimethylnaphthalene,



$$C_6H_4<\begin{matrix}\mathrm{CMe\!:\!C\cdot N_2Ph}\\ \mathrm{CMe\!:\!CH}\end{matrix};$$

with this formula, Cannizzaro and Andreocci's analytical results are in better accord than with that of the phenylhydrazone.

Dimethylnaphthaquinonitrole, $C_{12}H_{11}O_3N$, separates from ether as an oil which subsequently changes to yellow crystals, m. p. 99—100°.

Dimethylnaphthylazocarbonamide,  $C_6H_4<\begin{matrix}\mathrm{CMe\!:\!C\cdot N_2\cdot CO\cdot NH_2}\\ \mathrm{CMe\!:\!CH}\end{matrix}$ (compare Bamberger, *loc. cit.*), prepared by the action of semicarbazide on dimethylnaphtha-ψ-quinol, is deposited from aqueous alcohol as a pale orange-yellow, crystalline powder, m. p. 167—168° (decomp.), dissolves in hydrochloric acid giving a green coloration, and in concentrated sulphuric acid forming a green solution which changes to red, and is readily soluble in ether, acetic acid, or chloroform.

T. H. P.

d-Phellandrene in the Oil of Abies Siberica. IWAN SCHINDELMEISER (*Chem. Zeit.*, 1907, **31**, 759—760. Compare Abstr., 1903, i, 267; Bertram and Walbaum, Abstr., 1893, i, 659).—*d*-Phellandrene and dipentene have now been found, in addition to camphene and pinene previously observed, in the oil of *Abies sibirica*. The phellandrene nitrite, obtained from the fraction b. p. 169—172°, had m. p. 106—107°, $[a]_D - 46{\cdot}16°$, $D^{20} 1{\cdot}478$, and may have contained *l*-phellandrene nitrite (compare Wallach, Abstr., 1887, 967; Schreiner, Abstr., 1901, i, 600).

G. Y.

Presence of Amygdonitrile Glucoside [*l*-Mandelonitrile Glucoside] in Cerasus Padus. HENRI HÉRISSEY (*J. Pharm. Chim.*, 1907, [vi], **26**, 194—198).—From 1000 grams of young branches of *Cerasus Padus* covered with opening buds, the author has isolated about 0·3 gram of *l*-mandelonitrile glucoside, which was identified by its rotatory power, by its conversion into prulaurasin by means of a small quantity of baryta (compare Caldwell and Courtauld, Trans., 1907, **91**, 671), and by hydrolysis with hydrochloric acid which yields *l*-phenylglycollic acid.

T. H. P.

Production of Prulaurasin by the Action of a Soluble Enzyme on *iso*Amygdalin. HENRI HÉRISSEY (*J. Pharm. Chim.*, 1907, [vi], **26**, 198—201).—When yeast is mixed with 40 times its weight of distilled water and, after five or six hours, separated by filtration under pressure, washed with water, and dried at 33–34°, it is found to be capable of transforming *iso*amygdalin into prulaurasin (compare Caldwell and Courtauld, this vol., ii, 809).

Contrary to the statement of Caldwell and Courtauld (Trans., 1907, 91, 673), *iso*amygdalin is stable and non-hygroscopic and can be dried in the air. T. H. P.

Taxicatin, a New Glucoside from Taxus baccata. CHARLES LEFEBVRE (*J. Pharm. Chim.*, 1907, [vi], **26**, 241—254. Compare Chevallier and Lassaigne, *ibid.*, 1818, [ii], 4, 558; Lucas, *Arch. Pharm.*, 1856, [ii], **85**, 145; Marmé, *Chem. Centr.*, 1876, [iii], 7, 166; Hilger and Brandes, Abstr., 1890, 650; Thorpe, Trans., 1902, 81, 874).—*Taxicatin*, $C_{18}H_{22}O_7$, crystallises from alcohol in colourless needles, m. p. 169—170° (corr). Crystals obtained from aqueous solutions contain $2H_2O$. In 95% alcoholic solution, $a_D = -67{\cdot}25°$. It is decomposed by emulsin or by 2% sulphuric acid into dextrose and a substance readily soluble in ether and chloroform. When the glucoside is treated with a drop of nitric acid, a blue coloration is produced.

The yield of taxicatin was 35 grams from 70 kilos. of fresh substance. Twigs of *Taxus baccata* were found to contain both invertin and emulsin. N. H. J. M.

Presence of Aucubin in Different Species of Plantago. L. BOURDIER (*J. Pharm. Chim.*, 1907, [vi], **26**, 254—266).—The glucoside aucubin obtained by Bourquelot and Hérissey (Abstr., 1905, i, 364) from *Aucuba japonica* was found to be present in *Plantago major*, *P. media*, and *P. lanceolata*, and it probably occurs in *P. arenaria*, in *P. Cynops*, and in *P. Psyllium*. All varieties of *Plantago* were found to contain invertin and emulsin. N. H. J. M.

Two New Glucosides, Linarin and Pectolinarin. TIMOTHÉE KLOBB (*Compt. rend.*, 1907, **145**, 331—334).—It has already been shown (this vol., ii, 123) that the substance "linaric acid," isolated from *Linaria vulgaris*, is a glucoside which has been named linarin. It is now shown that the gelatinous substance, *pectolinarin*, discovered by Schlagdenhauffen in the same plant, is also a glucoside, differing in composition from linarin by a molecule of water. Linarin is very difficultly, pectolinarin easily, hydrolysed by hydrochloric acid. Both glucosides, on hydrolysis, give a reducing sugar and a mixture of *linaric* and *anhydrolinaric phenols*. Linarin is lævorotatory; when dissolved in hydrochloric acid to a 1·2% solution, it has a $-61{\cdot}8°$.

Pectolinarin is a straw-yellow, amorphous substance, m. p. 188—190° (on Maquenne block), which is transformed into crystallised linarin by prolonged boiling with water. Both linarin and pectolinarin, when dissolved in normal alkali, are, in twenty-four hours, transformed into β-modifications. β-Linarin, on hydrolysis with hydrochloric acid, gives *anhydrolinaric phenol* in straw-yellow needles, m. p. 267—268°, which dissolves in sodium hydroxide solution giving a golden-yellow liquid, but no green flakes, and forms an *acetyl* derivative, $C_{19}H_9O_6Ac_3$. β-Pectolinarin, by similar treatment, gives *linaric phenol* in lemon-yellow crystals, m. p. 245°. This dissolves in sodium hydroxide to a solution which gives a deep green, flocculent precipitate in contact with air (difference from anhydrolinaric phenol). Assuming that the sugar formed is a hexose, the author suggests, provisionally, that the hydrolysis of α-linarin should be represented by the equation:

$$C_{50}H_{50}O_{25} = \underset{\text{Linaric phenol.}}{C_{19}H_{14}O_7} + \underset{\text{Anhydrolinaric phenol.}}{C_{19}H_{12}O_6} + 2C_6H_{12}O_6.$$

E. H.

Rhinanthin. MARCEL MIRANDE (*Compt. rend.*, 1907, **145**, 439—442).—The glucoside rhinanthin, $C_{58}H_{52}O_{40}$, which is relatively rare in *Rhinanthus*, *Euphrasia*, and *Odontites*, occurs abundantly in the Orobanches and *Phelipæa*. A detailed description is given of the microchemical reactions of the glucoside, and also of the parts of *Orobanchehederæ* and *Pedicularis comosa* in which it is found.

In the Orobanches, the quantity of rhinanthin diminishes as the seed ripens and as the stem dries. When the stem is dry, it appears no longer to contain the glucoside.

Rhinanthin is interesting as a glucoside, which is localised specially in the wood of certain generally parasitic plants. E. H.

Chlorophyll. IV. Yellow Substances which accompany Chlorophyll. RICHARD WILLSTÄTTER and WALTER MIEG (*Annalen*, 1907, **355**, 1—28. Compare this vol., i, 784).—An investigation of two yellow pigments, carrotene and xanthophyll, which occur together with chlorophyll in green leaves.

Carrotene, obtained by extracting stinging-nettle leaves with light petroleum, crystallises in copper-coloured leaflets which appear red by transmitted light, and is undoubtedly identical with the carrotene obtained from carrots. The results of analysis and molecular weight determinations show that it has the formula $C_{40}H_{56}$, and not $C_{26}H_{38}$ as assigned to it by Arnaud (Abstr., 1885, 670; 1886, 711; 1887, 859). It is probable that erythrophyll (Bongarel, this Journ., 1877, ii, 790) and chrysophyll (Schunck, Abstr., 1889, 279) are identical with carrotene, and that Husemann's carroten (*Annalen*, 1861, **117**, 200) is a definite oxidation product of carrotene, $C_{40}H_{56}O_2$, isomeric with xanthophyll.

Carrotene absorbs oxygen to the extent of 34·3% of its weight, being converted into a colourless substance (compare Arnaud, Abstr., 1890, 285). It likewise combines with iodine, forming *carrotene iodide*, $C_{40}H_{56}I_2$, which crystallises in rosettes of dark violet prisms and sinters and decomposes at 140—170°.

Xanthophyll, which accompanies chlorophyll in the alcoholic extract of leaves, is similar to carrotene in appearance, but differs from it in that the crystals appear yellow by transmitted light. Molecular weight determinations and analysis show that it has the formula $C_{40}H_{56}O_2$. It combines with methyl and ethyl alcohols, forming the *substances* $C_{40}H_{56}O_2,CH_4O$ and $C_{40}H_{56}O_2,C_2H_6O$; the alcohol is slowly given off in a vacuum. Xanthophyll is an indifferent substance, and reacts neither as an alcohol, acid, nor ketone. Like carrotene, it readily absorbs oxygen to the extent of 36·55% of its weight. From the oxidised material, the *compound*, $C_{40}H_{56}O_{18}$, was isolated in the form of a white, crystalline powder, which swells up at 100° and melts slowly at 140°.

Xanthophyll readily unites with iodine, forming *xanthophyll iodide*, $C_{40}H_{56}O_2I_2$, which crystallises in tufts of thin, dark violet prisms with a metallic lustre.

The authors maintain that it is impossible by the methods of Kraus, Sorby (*Proc. Roy. Soc.*, 1873, 21, 442), and Marchlewski and Schunck (Trans., 1900, 77, 1080) to obtain chlorophyll free from carrotene, and they show, further, that Kraus's method is superior to that of Sorby for the separation of xanthophyll from chlorophyll.

W. H. G.

Studies in the Chlorophyll Group. T. Kózniewski and Leon Marchlewski (*Annalen*, 1907, **355**, 216—234. Compare Willstätter and Hocheder, this vol., i, 784; Tsvett, *ibid.*, 787).—Phylloxanthin, extracted from *Ficus repens* and carefully freed from phyllocyanin, is dissolved in 90% alcohol, and potassium hydroxide added to make a 6% solution. After being heated for thirty minutes, the products are isolated and examined by Willstätter's method (this vol., i, 69). The ethereal solution is extracted with 2%, 5%, 10%, and 25% solutions of hydrochloric acid. The 10% extract has a reddish-brown colour; the ethereal extract of the diluted solution is red and strongly fluorescent, whilst the residual hydrochloric acid solution is dark green and non-fluorescent, and on evaporation leaves a dark green substance which is called *phylloxantrubin*, the spectrum of which is very similar to that of the original phylloxanthin. From the 25% extract is obtained a neutral substance, called *phylloxantverdin*, the spectrum of which in ethereal solution shows two absorption bands in the red, a faint one in the orange, and a stronger one in the bluish-green.

Alkachlorophyll is converted by alcoholic hydrogen chloride into the so-called phyllotaonin ethers, which yield on hydrolysis a phyllotaonin which should be identical with that obtained by Schunck by the action of alkalis on phyllocyanin. Schunck's results of the spectroscopic examination of his phyllotaonin in ethereal solution, according to which the substance shows five absorption bands which become six after treatment with acid, have been criticised adversely by Marchlewski, who found that crystalline phyllotaonin in ethereal solution yields a six-banded spectrum without treatment by acids. The authors have reinvestigated the subject, working on larger quantities of materials. A mixture of methyl and ethyl phyllotaonin (0·67 gram) is heated for twenty-five minutes with 3% alcoholic sodium hydroxide, and the products of hydrolysis are isolated, dissolved in ether, and extracted with 2%, 4%, 7%, 11%, and 15% hydrochloric acid. The phyllotaonin produced by the hydrolysis is present mainly in the 4% extract, and is obtained in the form of a steel-blue mass (0·55 gram). The spectrum of its ethereal solution, which is olive-green with red fluorescence, contains, before evaporation, five bands and recalls that of phyllocyanin; by the evaporation of its ethereal solution, phyllotaonin is changed incompletely into another substance called allo*phyllotaonin*, the change being complete when phyllotaonin is evaporated repeatedly with chloroform. From the incompletely transformed product, a substance can be obtained the six-banded spectrum of which is identical with that of Schunck's crystalline phyllotaonin.

*allo*Phyllotaonin is a feebly basic substance, dissolves sparingly in ether forming a non-fluorescent solution the spectrum of which is identical with that of crystalline ethylphyllotaonin, from which substance *allo*phyllotaonin differs by its solubility in very dilute aqueous sodium hydroxide. When its solution in sodium hydroxide is acidified immediately, the substance is recovered unchanged; if some time elapses before acidifying, a substance is obtained the spectrum of which is identical with that of Schunck's crystalline phyllotaonin; if the alkaline solution is boiled before acidifying, the *allo*phyllotaonin is converted into the phyllotaonin obtained as above by the hydrolysis of the phyllotaonin ethers.

These results indicate that Schunck's crystalline phyllotaonin, the spectrum of which shows six bands, is a mixture of *allo*phyllotaonin and the authors' phyllotaonin, the spectrum of which has five absorption bands. This deduction is supported by the facts that a mixture of the dilute ethereal solutions of *allo*phyllotaonin and phyllotaonin has the same spectrum as Schunck's crystalline phyllotaonin, and that from the latter in ethereal solution 7% hydrochloric acid extracts the authors' phyllotaonin, 11% and 15% hydrochloric acid a mixture of phyllotaonin and *allo*phyllotaonin, whilst *allo*phyllotaonin alone remains in the residual ethereal solution.

Little can be said concerning the nature of the change of phyllotaonin into *allo*phyllotaonin, and vice versa. Acids alone do not cause the former change. The fact that phyllotaonin changes into *allo*phyllotaonin after prolonged keeping in a dry atmosphere indicates that the change may be one of anhydride formation.

C. S.

Chlorophyll. LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1907, **5**, 344—345).—Largely a polemical reply to Tsvett (this vol., i, 787). It is pointed out that β-chlorophyllan cannot be identical with phylloxanthin, as the absorption spectra of the two substances are different.

J. J. S.

The Dye of Antique Purple from Murex brandaris. PAUL FRIEDLÄNDER (*Monatsh.*, 1907, **28**, 991—996).—A short account is given of the work of various authors on the purple of the ancients. The dyes obtained by Schunck (Trans., 1879, **35**, 589; 1880, **37**, 613) and Letellier (Abstr., 1889, 1207; 1890, 1452) cannot be the purple of the Romans, as *Purpura lapillus* does not occur in the Mediterranean.

A small amount of a pure purple *dye* has been obtained now from *Murex brandaris*; it contains nitrogen, but not sulphur, forms dark violet crystals, and in its appearance, the colour of its vapour, and absorption spectrum resembles indigotin, but is distinguished from this by its more sparing solubility, by giving with cold concentrated sulphuric acid a reddish-violet coloration, becoming brownish-violet when heated, and yielding a reddish-violet precipitate on addition of water. When treated with fuming sulphuric acid, the purple dye yields a blue, soluble *sulphonic acid*, and on reduction in alkaline solution forms a slightly yellow solution from which it separates as a reddish-violet, flocculent precipitate on exposure to air. These properties show that the purple dye, whilst closely resembling indigotin and thioindigotin, is not identical with either (compare Abstr., 1906, i, 378; this vol., i, 334). G. Y.

Monocarboxylic Acids of Thiophen. GERARDUS L. VOERMAN (*Rec. trav. chim.*, 1907, **26**, 293—310).—The author has made various physico-chemical measurements of thiophen-2- and 3-carboxylic acids, and of the isomeric *a*-acid of Meyer (V. Meyer, "Die Thiophengruppe," Brunswick, 1888), in order to ascertain the relation of the *a*-acid to the 2- and 3-acids.

The melting-point curve for mixtures of the 2- and 3-acids shows that the two acids form two series of homogeneous mixed crystals, with a gap between 25% and 60·5% of the 3-acid. The electrical conductivity of the mixtures was also determined.

[F. M. JAEGER.—Crystals of the 2-acid have only rudimentary ends and cannot be defined morphologically, but those of the 3-acid are monoclinic. The acids form a series of isodimorphous mixtures, with a gap from 22·5% to 61—62% of the 3-acid.]

Meyer's *a*-acid represents one term in the series of mixed crystals, and contains 82—83% of the 2-acid and 17—18% of the 3-acid. Preliminary experiments indicate that it can be separated into its components by crystallisation. T. H. P.

Crystalline Double Iodide of Bismuth and Strychnine. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, **12**, 357).—Bismuth and strychnine form a crystalline *double iodide* which is well suited for the microchemical identification of strychnine. The reagent is prepared by adding a large excess of potassium iodide to a very dilute solution of bismuth chloride, containing a small amount of alcohol, and acidifying with hydrochloric acid. If this is added to a solution of a strychnine salt, there is formed a chocolate-brown precipitate, which rapidly becomes crystalline, and glistens when agitated. Under the microscope, the precipitate appears as a matted mass of needles together with isolated, flame-coloured, dichroic, prismatic crystals.

G. Y.

Double Iodide of Bismuth and Cocaine. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1907, **12**, 358).—The *double iodide* of bismuth and cocaine is obtained usually as a brick-red, amorphous precipitate, but if precipitated by means of the reagent described in the preceding abstract and heated becomes crystalline after some hours. Under the microscope, the precipitate appears as matted, fiery-red needles, and serves for the microchemical identification of cocaine.

The precipitate dissolves in alcohol forming an orange-yellow solution; it does not crystallise from this solution on evaporation, but does so after some hours from an aqueous solution in presence of an excess of bismuth. G. Y.

Picrolonates of Certain Alkaloids. WILLIAM H. WARREN and R. S. WEISS (*J. Biol. Chem.*, 1907, 3, 327—338).—The following numbers give the number of grams of picrolonic acid (4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone) which dissolve in 1 c.c. of the respective solvents: water, 0·0017; alcohol, 0·0209; ether, 0·005; benzene, 0·0024; chloroform, 0·015; ethyl acetate, 0·041; amyl alcohol, 0·0056. An alcoholic solution of the acid may be used for precipitating alkaloids, and the reaction is more delicate than that with picric acid, but not to a very marked extent. The picrolonates of the following alkaloids are described: coniine, pale yellow, large rhombohedra, m. p. 195·5° (decomp.); nicotine, long prismatic needles, m. p. 213°; strychnine, crystalline plates, or rectangular prisms, m. p. about 275° (decomp.); brucine, cubical crystals, m. p. 256° (decomp.); morphine, broad, flat needles, readily soluble in alcohol, m. p. 186·5°; codeine, deep yellow rosettes of short prisms, m. p. 219°; atropine, pointed crystals, m. p. 194°; quinine, hair-like needles, m. p. 225°; hydrastine, long, flat needles, m. p. 220°. All the salts contain 1 mol. of the base combined with one of picrolonic acid, with the exception of the quinine salt, which contains 2 mols. of the acid.

Picrolonates of cocaine, aconitine, and caffeine have not been obtained.

Brucine picrate exists in two modifications, a yellow and an orange-red; the former is transformed into the latter when heated at 213°. J. J. S.

Bebeerine. HERMANN HILDEBRANDT (*Archiv. exp. Path. Pharm.*, 1907, 57, 279—284).—Scholtz has shown that bebeerine and pelosine, formerly known only in the amorphous state, may be crystallised from methyl alcohol and that they may be recovered again in the amorphous condition by means of chloroform. Buxine, from *Buxus sempervirens*, does not show these properties, and is therefore distinct from the two former compounds. The chemical constitution of the crystalline and the amorphous bebeerine is the same, $OH \cdot C_{16}H_{14}O(OMe)NMe$. It is lævorotatory. Recently in investigating the alkaloidal constituents of the roots of *Pareira brava* he obtained a dextrorotatory, crystalline substance having the same specific rotation and constitution as bebeerine, and the same m. p. as the latter when crystalline. By admixture in chloroform, the racemic compound, m. p. 300°, which could also be isolated from the plant, was obtained. The physiological action of the following compounds was investigated. The amorphous and crystalline forms of *d*- and *l*-bebeerine, the racemic modification in small quantities, the methiodide, and commercial bebeerine sulphate. The latter substance contains other alkaloidal constituents besides bebeerine. In frogs, no results could be obtained bearing on the differences of effect between the various bases. The general effect was that of curare. In white mice, subcutaneous injection of a 3% solution of the chloride gave results dependent on the direction of rotation of the alkaloid. The racemic compound behaved as a molecular mixture.

With dogs, using the *d*-base, a dose of the crystalline form, equivalent to a lethal dose of the amorphous form, has no effect. The dextro-crystalline base is much more toxic to cats than dogs. The amorphous form of the *l*-base is much more toxic than the crystalline form to dogs. Bebeerine was recovered from the urine of the animals experimented upon partly as an easily decomposed combination with glycuronic acid. Molecular weight determinations point to the simple molecular formula $C_{18}H_{21}O_3N$ for both the amorphous and the crystalline modifications.

G. S. W.

[Carnosine.] Wladimir von Gulewitsch (*Zeitsch. physiol. Chem.*, 1907, **52**, 527—528).—The reactions of carnosine with silver nitrate and alkalis are as previously described by Gulewitsch and Amiradžibi (Abstr., 1900, i, 516). When equivalent amounts of carnosine and silver nitrate are used, the addition of ammonia, either in large or small amounts, produces no precipitate (compare Kutscher, this vol., i, 337).

J. J. S.

Chemical Properties of Amanita-toxin. Hermann Schlesinger and William W. Ford (*J. Biol. Chem.*, 1907, **3**, 279—283).—When the aqueous extract of *Amanita phalloides* is mixed with alcohol, the hæmolytic glucoside, phallin (this vol., ii, 192), is precipitated, and the heat-resistant amanita-toxin is found in the alcoholic filtrate. This toxin can produce in animals the lesions found in man, including hæmorrhage, necrosis, and especially fatty degeneration. The toxin is readily soluble in water, but only sparingly so in hot absolute alcohol; its solutions may be boiled for some time without losing its toxic properties. It is slowly affected by dilute acids at the ordinary temperature and rapidly by boiling acids. It does not react with any of the ordinary reagents for alkaloids with the exception of phosphotungstic acid. It appears to be neither glucoside, alkaloid, nor protein in the generally accepted sense of these terms. It contains both nitrogen and sulphur, the latter in the form of conjugate sulphuric acid. When heated with solid potassium hydroxide, it yields indole and pyrrole.

J. J. S.

Aporeine and other Alkaloids of Papaver dubium. II. Vittorio Pavesi (*Gazzetta*, 1907, **37**, i, 629—636).—Contrary to what was previously stated (Abstr., 1905, i, 368), aporeine is deposited from solvents as an amorphous, resinous, almost colourless mass, showing a faint, whitish-blue fluorescence, and is readily soluble in ether, chloroform, carbon disulphide, ethyl acetate, light petroleum, or alcohol, in the last of which it has a slight alkaline reaction towards litmus. The crystalline salts formed with the mineral acids have an acid reaction. The hydrochloride, $C_{18}H_{16}O_2N,HCl$, *sulphate*, *nitrate*, *acetate*, and *platinichloride*, $(C_{18}H_{16}O_2N)_2,H_2PtCl_6$, have been prepared. Aporeine salts are precipitated by most of the general alkaloid reagents, to some of which they are extremely sensitive. A number of reactions of aporeine are given.

On exposing a solution of aporeine hydrochloride to the action of sunlight for a fortnight and extracting with ether, another base, *aporegenine*, is obtained, which crystallises in masses of white needles, but could not be obtained in a pure state.

Aporeine is accompanied, in the latex of *Papaver dubium*, by another base, *aporeidine*, which crystallises from ether in bundles of minute, white needles, m. p. 124—125° (somewhat impure). Various reactions of aporeidine are described. T. H. P.

The Poison Plants of Western Australia. Edward A. Mann and Walter H. Ince (*Proc. Roy. Soc.*, 1907, 79, *B*, 485—491).—The authors have investigated the poisonous plants of Western Australia and have isolated the new alkaloids, *cygnine*, from the "York Road" poison plant, *Gastrolobium calycinum*, and *lobine* from the "Box" poison plant, *Oxylobium parviflorum*. In the preparation of cygnine, the material obtained by alcoholic extraction when treated with lead acetate and then tannic acid, gives a residue which crystallises from hydrochloric acid and alcohol as a mixture of needle-shaped and cubical crystals. The former are very toxic; the latter appear to be a degradation product of the alkaloid, and have an acid reaction. Their composition would indicate the formula $C_{12}H_{16}O_3$.

The acicular crystals are the hydrochloride of an alkaloid $C_{12}H_{22}O_3N_2$. They are unstable, undergoing spontaneous decomposition if left moist or heated above 30°. One hundred c.c. of water dissolve 1·932 grams at 15°. The aqueous solution gives the usual alkaloidal reactions. Physiological experiments showed the alkaloid to be a powerful poison, belonging to that group of which the principal member is strychnine.

Lobine was obtained in a similar way and is a very similar substance. It is slightly more stable, and has the composition $C_{23}H_{31}O_4N_3$. Like cygnine, its hydrochloride when heated yields a non-nitrogenous substance, crystallising in cubes, and a nitrogenous uncrystallisable compound. The form in this case has the composition $C_9H_{14}O_3$.

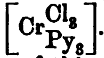
Some other substances were obtained from the "York Road" poison plant besides cygnine.

Cygnic acid, $C_{10}H_{10}O_4$, was recovered from the lead precipitate obtained during the clearing of the alcoholic extracts. It gives a stable *ammonium* salt which is precipitated as a crystalline powder by addition of alcohol, and when analysed gives figures corresponding with $C_{10}H_8O_4(NH_4)_2$. The *lead*, *silver*, and *barium* salts are insoluble.

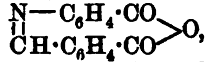
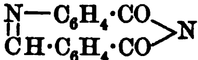
Gastrolobic acid, $C_7H_{10}O_5,H_2O$, is obtained from the same source as cygnic acid, and forms a stable *sodium* salt.

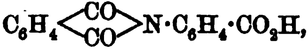
Gastrolobin is a vegetable gelatinoid. When the lead acetate precipitate is suspended in water and decomposed by passing hydrogen sulphide, the filtrate has a viscous character. The addition of absolute alcohol brings about the precipitation of a flocculent substance, insoluble in water. It does not reduce Fehling's solution, and is precipitated by tannic acid, dilute sulphuric acid, and sodium carbonate. An analysis shows its composition to be in accordance with the formula $C_6H_{10}O_5$. The oxidation product resulting from treatment with nitric acid gives the pyrrole test for mucic acid. The substance probably belongs to that ill-defined family of vegetable carbohydrate gelatinoids of which agar-agar is the best known member.

Cygnose, $C_6H_{12}O_6$, is isolated from the solution, after removal of the gastrolobin by means of lead acetate, by means of its *osazone*, which crystallises from alcohol in yellow needles, m. p. 179°. The sugar is optically inactive, both before and after inversion. It is not fermented by yeast. G. S. W.

Constitution of Tripyridinechromium Trichloride. Paul Pfeiffer (*Zeitsch. anorg. Chem.*, 1907, **55**, 97—100).—The ordinary method for determining constitutions cannot be applied to tripyridinechromium trichloride, $CrCl_3,3Py$, previously prepared by the author (Abstr., 1900, i, 559) on account of its complete insolubility in water. As, however, it is soluble in concentrated nitric acid and precipitated unchanged by water, it is considered improbable that any of the chlorine atoms are ionised, and, since it is soluble in such organic solvents as pyridine and glycol, its constitution is probably represented by the formula  $\left[\mathrm{Cr}^{\mathrm{Cl_3}}_{\mathrm{Py_3}}\right]$.

The behaviour of this compound towards nitric acid and water may be taken advantage of to obtain it in a pure condition. G. S.

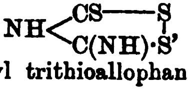
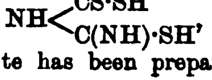
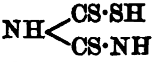
Condensation Products of Phthalonic Acid with Anthranilic Acid. Rosario Spallino (*Gazzetta*, 1907, **37**, ii, 151—154).—When phthalonic acid is heated with anthranilic acid, it decomposes with formation of benzaldehyde-*o*-carboxylic acid, which condenses with the anthranilic acid yielding the *compound*  $\begin{matrix}N-C_6H_4\cdot CO\\ \| \\ CH\cdot C_6H_4\cdot CO\end{matrix}>O$, crystallising from alcohol in slender, white needles, m. p. 215°, and having the normal molecular weight in boiling alcohol. When heated with alcoholic ammonia in a closed tube at 100°, this substance is converted into the *compound*  $\begin{matrix}N-C_6H_4\cdot CO\\ \| \\ CH\cdot C_6H_4\cdot CO\end{matrix}>NH$, which separates in long, white needles, m. p. 240°, and is soluble in alcohol. The interaction of phthalonic and anthranilic acids also yields the compound



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_6H_4\cdot CO_2H,$$

which owes its presence to the action on the anthranilic acid of the phthalic anhydride produced in the decomposition of phthalonic acid. T. H. P.

Derivatives of Perthiocyanic Acid and of Cyanoimidodithiocarbonic Acid. Synthesis of New Triazoles. Emil Fromm and D. von Göncz (*Annalen*, 1907, **355**, 196—215).—Hantzsch and Wolvekamp's perthiocyanic acid (Abstr., 1904, i, 718) may be regarded as the disulphide of a dihydric mercaptan, which in its tautomeric form is trithioallophanic acid,

$$NH<\begin{matrix}CS-S\\ \quad\ \ |\\ C(NH)\cdot S\end{matrix},\quad NH<\begin{matrix}CS\cdot SH\\ C(NH)\cdot SH\end{matrix},\quad NH<\begin{matrix}CS\cdot SH\\ CS\cdot NH_2\end{matrix}$$

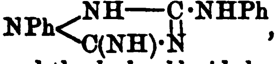
Benzyl trithioallophanate has been prepared by Fromm (Abstr., 1895, i, 605) from *as*-phenylmethyldithiobiuret, which, in its turn, is obtained from perthiocyanic acid. This relationship between perthiocyanic acid and trithioallophanic acid is supported by the following results.

Dibenzyl cyanoiminodithiocarbonate, $(C_7H_7\cdot S)_2C\colon N\cdot CN$, m. p. 82°, is obtained by the reaction in alcoholic solution between benzyl chloride and the potassium salt, which Hantzsch and Wolvekamp have prepared by the action of potassium hydroxide on perthiocyanic acid (*loc. cit.*). The successive action of hydrogen sulphide and of dry ammonia on a cold alcoholic solution of the dibenzyl ester leads to the formation of benzyl mercaptan and benzyl trithioallophanate.

Dibenzyl cyanoiminodithiocarbonate is converted by cold alcoholic ammonia into benzyl mercaptan and *amino-ψ-benzylthiocarbamide cyanide* (*benzyl cyanoiminothiocarbamate*), $C_7H_7S\cdot C(NH_2)\colon N\cdot CN$, m. p. 158°, which is decomposed by boiling concentrated hydrochloric acid forming benzyl thioallophanate (compare Fromm, Abstr., 1895, ii, 461). Aniline and *o*- and *p*-toluidines react in a similar manner with dibenzyl cyanoiminodithiocarbonate in hot alcohol, forming benzyl esters of cyanoiminothiocarbamates in which a hydrogen atom of the amino-group is replaced by the aryl group of the amine; these compounds have been already prepared by Fromm by the action of sodium hydroxide and benzyl chloride on substituted thiobiurets. Benzidine and dibenzyl cyanoiminodithiocarbonate react to form the *compound* $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot C(SC_7H_7)\colon N\cdot CN$, which begins to decompose at 190°, but is not fused at 280°.

Phenylhydrazine and dibenzyl cyanoiminodithiocarbonate react energetically to form Fromm and Schneider's 5-amino-3-thiobenzyl-1-phenyl-1 : 2 : 4-triazole (Abstr., 1906, i, 714), the *diacetyl* derivative of which has m. p. 228—229°.

Ammonia or aniline reacts with benzyl cyanoiminophenylthiocarbamate, $C_7H_7S\cdot C(NHPh)\colon N\cdot CN$, at 110—120°, with the elimination of benzyl mercaptan, but a pure product has not been isolated. At the same temperature, phenylhydrazine in excess reacts to form a *base*, m. p. 148°, together with a small quantity of an *isomeride*, m. p. 166°; at 180°, the latter is the main product. These bases, which are stable towards boiling hydrochloric acid, are guanazole derivatives; the former is regarded as 5-amino-3-anilino-1-phenyl-1 : 2 : 4-triazole,



$$\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{NH{-}{-}C\cdot NHPh}\\ \qquad\qquad\| \\ \mathrm{C(NH)\cdot N}\end{array}$$

, the *acetyl* derivative of which has m. p. 189°, and the *hydrochloride* has m. p. 275°. The latter is sparingly soluble, and changes by heating with phenylhydrazine at 180° to the very soluble *hydrochloride* of the isomeric base, m. p. 166°, which is regarded as 3-amino-5-anilino-1-phenyl-1 : 2 : 4-triazole; the *acetyl* derivative has m. p. 166°. C. S.

Action of Cyanogen Halides on Phenylhydrazine. Guido Pellizzari (*Gazzetta*, 1907, 37, i, 611—623).—In ethereal solution, cyanogen chloride reacts with phenylhydrazine to form anilcyanamide or phenylaminocyanamide, NHPh·NH·CN (Abstr., 1892, 1323). The author now finds that, in aqueous solution, these two compounds interact in two ways, a small proportion of phenylaminocyanamide being formed, but the main product being aminophenylcyanamide formed according to the equation: $2NH_2{\cdot}NHPh + CNBr = NH_2{\cdot}NPh{\cdot}CN + NH_2{\cdot}NHPh,HBr$. The phenylaminocyanamide formed undergoes transformation, yielding (1) phenylsemicarbazide, formed by the reaction $NHPh{\cdot}NH{\cdot}CN + H_2O = NHPh{\cdot}NH{\cdot}CO{\cdot}NH_2$, and (2) diphenyldiaminoguanidine hydrobromide, formed by the addition of phenylhydrazine hydrobromide, $NHPh{\cdot}NH{\cdot}CN + NH_2{\cdot}NHPh,HBr = NH{:}C(NH{\cdot}NHPh)_2,HBr$.

Aminophenylcyanamide or *a-cyanophenylhydrazide*, $NH_2{\cdot}NPh{\cdot}CN$, crystallises from alcohol in shining, white plates, m. p. 89°, dissolves in water, benzene, or ether, has the normal molecular weight in boiling alcohol or benzene, and reduces ammoniacal silver nitrate or Fehling's solution. It has, however, no basic properties, and does not dissolve in acids or form a salt with picric acid.

Diphenyldiaminoguanidine hydrobromide, $NH{:}C(NH{\cdot}NHPh)_2,HBr$, is deposited from alcohol in round masses of reddish crystals, m. p. 178—180° (decomp.), and dissolves in water with a red coloration which disappears on the addition of an acid. The picrate, $C_{13}H_{15}N_5,C_6H_3O_7N_3$, crystallises from alcohol in minute needles, m. p. 170° (decomp.).

Benzylideneaminophenylcyanamide, $CN{\cdot}NPh{\cdot}N{:}CHPh$, prepared by the interaction of aminophenylcyanamide and benzaldehyde in water containing a small quantity of hydrochloric acid, separates from alcohol in shining crystals, m. p. 103°, and dissolves sparingly in water.

Aminophenylcarbamide (*a-phenylsemicarbazide*), $NH_2{\cdot}NPh{\cdot}CO{\cdot}NH_2$, obtained by hydrolysing aminophenylcyanamide by means of boiling 10% potassium hydroxide, is deposited from alcohol in shining crystals, m. p. 120°, has the normal molecular weight in boiling alcohol, and reduces Fehling's solution and ammoniacal silver nitrate solution containing potassium hydroxide. It has basic properties, and dissolves in acids in the cold.

Benzylideneaminophenylcarbamide, $CHPh{:}N{\cdot}NPh{\cdot}CO{\cdot}NH_2$, prepared by the action of benzaldehyde on aminophenylcarbamide in presence of an acid, crystallises from alcohol in white needles, m. p. 154°, and is moderately soluble in alcohol.

Aminophenylthiocarbamide, $NH_2{\cdot}NPh{\cdot}CS{\cdot}NH_2$, obtained by the interaction of aminophenylcyanamide and ammonium hydrosulphide, crystallises from water in striated laminæ, m. p. 153°, dissolves to a moderate extent in alcohol, and combines with aldehydes and ketones, forming readily crystallisable compounds.

Benzylideneaminophenylthiocarbamide, $CHPh{:}N{\cdot}NPh{\cdot}CS{\cdot}NH_2$, separates from benzene in large transparent crystals containing $1\frac{1}{2}C_6H_6$, m. p. 65—70°, or, when free from benzene, 163°; it is readily soluble in alcohol and sparingly so in water. T. H. P.

Aromatic Nitro-derivatives. ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 133—138).—In continuation of his previous investigations (Ciusa and Agostinelli, Abstr., 1906, i, 891), the author has studied the action of picryl chloride on acetonazine, and on acetone-*s*-trinitrophenylhydrazone, -2 : 4-dinitrophenylhydrazone, and

-*p*-nitrophenylhydrazone. Picryl chloride acts on acetonazine liberating 1 mol. of acetone and forming acetonetrinitrophenylhydrazone, on which it exerts no further action; with the dinitro- and mononitrophenylhydrazones of acetone, it reacts readily, liberating acetone and forming 2 : 4 : 6 : 2′ : 4′-pentanitrohydrazobenzene and 2 : 4 : 6 : 4′-tetranitrohydrazobenzene respectively. The behaviour of 1-chloro-2 : 4-dinitrobenzene is quite analogous to that of picryl chloride.

Acetonetrinitrophenylhydrazone, prepared from picryl chloride and acetonazine, has m. p. 130° and not 125° as was stated by Purgotti (Abstr., 1895, i, 27) and Curtius and Dedichen (Abstr., 1895, i, 29).

2 : 4 : 6 : 2′ : 4′-*Pentanitrohydrazobenzene*,

$$C_6H_2(NO_2)_3\cdot NH\cdot NH\cdot C_6H_3(NO_2)_2,$$

crystallises from a mixture of ethyl acetate, alcohol, and a few drops of acetic acid in microscopic, golden-yellow plates, m. p. 226° (decomp.), and gives an intense violet coloration with even a trace of alkali.

2 : 4 : 6 : 4′-*Tetranitrohydrazobenzene*,

$$C_6H_2(NO_2)_3\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2,$$

is deposited from a mixture of ethyl acetate and alcohol in yellow, acicular crystals, m. p. 210°, and gives an intense coloration with a trace of alkali.

The action of 1-chloro-2 : 4-dinitrobenzene on acetonazine yields acetone-2 : 4-dinitrophenylhydrazone, m. p. 128° (compare Curtius and Dedichen, Abstr., 1895, i, 29; Fischer and Ach, Abstr., 1890, 40; and Purgotti, Abstr., 1895, i, 27).

The action of 1-chloro-2 : 4-dinitrobenzene on benzylideneazine yields benzaldehyde-2 : 4-dinitrophenylhydrazone.

2 : 4-*Dinitrodiphenylamine*, $NHPh\cdot C_6H_3(NO_2)_2$, obtained by the action of 1-chloro-2 : 4-dinitrobenzene on benzylideneaniline, separates from alcohol in red crystals, m. p. 156°. T. H. P.

Condensation Products of Aminophenylcyanamide with Aldehydes and Ketones. LUIGI ROLLA (*Gazzetta*, 1907, 37, i, 623—629. Compare preceding abstract).—Aminophenylcyanamide, $NH_2\cdot NPh\cdot CN$, reacts with aldehydes and ketones and even with compounds such as quinone and alloxan, yielding derivatives analogous to phenylhydrazones and having the structure $R\colon N\cdot NPh\cdot CN$. The reaction proceeds best in alcoholic solution and in presence of a small quantity of hydrochloric acid.

Ethylideneaminophenylcyanamide (*acetaldehydecyanophenylhydrazone*), $CHMe\colon N\cdot NPh\cdot CN$, separates from alcohol in white crystals, m. p. 45°, and dissolves in ether, benzene, or water.

Salicylideneaminophenylcyanamide (*salicylaldehydecyanophenylhydrazone*), $OH\cdot C_6H_4\cdot CH\colon N\cdot NPh\cdot CN$, separates from alcohol as a white, indistinctly crystalline substance, m. p. 132°, and is readily soluble in benzene or ether.

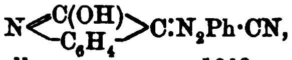
Nitrobenzylideneaminophenylcyanamide (*nitrobenzaldehydecyanophenylhydrazone*), $NO_2\cdot C_6H_4\cdot CH\colon N_2Ph\cdot CN$, crystallises from alcohol in white, opaque leaflets, m. p. 163°, and dissolves in benzene.

Vanillideneaminophenylcyanamide (*vanillincyanophenylhydrazone*),

$OH{\cdot}C_6H_3(OMe){\cdot}CH{:}N_2Ph{\cdot}CN$, forms white crystals, m. p. 118°, and dissolves in alcohol or ether.

Furfurylideneaminophenylcyanamide (*furfuraldehydecyanophenylhydrazone*), $C_6OH_3{\cdot}CH{:}N_2Ph{\cdot}CN$, is deposited from alcohol in minute, white crystals, m. p. 98°, and is soluble in ether or benzene.

Acetophenonecyanophenylhydrazone, $CPhMe{:}N_2Ph{\cdot}CN$, separates from alcohol as a felted mass of minute, white crystals, m. p. 67°, and dissolves in ether or benzene.

Isatincyanophenylhydrazone, 
$N\Big<\genfrac{}{}{0pt}{}{C(OH)}{C_6H_4}\Big>C{:}N_2Ph{\cdot}CN$, separates from alcohol as a voluminous, yellow mass, m. p. 191°, and is readily soluble in ether or benzene.

Benzil-monocyanophenylhydrazone, $COPh{\cdot}CPh{:}N_2Ph{\cdot}CN$, separates from alcohol in pale yellow crystals, m. p. 168°.

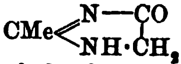
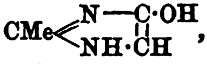
Benzoquinonedi-cyanophenylhydrazone, $C_6H_4(N_2Ph{\cdot}CN)_2$, crystallises from alcohol in red scales with golden-yellow lustre, m. p. 178°, and dissolves readily in ether or benzene.

Alloxancyanophenylhydrazone, $C_4H_2O_3N_2{:}N_2Ph{\cdot}CN$, separates as a voluminous, straw-yellow precipitate, m. p. 286°.

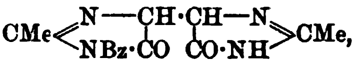
With ethyl acetoacetate, benzophenone, and tetramethyldiaminobenzophenone, aminophenylcyanamide yields oily products, whilst with the sugars no compounds could be prepared. T. H. P.

Preparation of Quinazoline Derivatives. HERMANN FINGER (*J. pr. Chem.*, 1907, [ii], 76, 97. Compare Abstr., 1906, i, 901).—Acetiminoethyl ether and benziminoethyl ether condense with isatoic acid with the elimination of carbon dioxide and alcohol, and the formation of 4-keto-2-methyldihydroquinazoline, $C_9H_8ON_2$, and 4-keto-2-phenyldihydroquinazoline, $C_{14}H_{10}ON_2$, respectively. W. H. G.

Action of Imino-ethers on Amino-esters. HERMANN FINGER [and, in part, SCHUPP and W. ZEH] (*J. pr. Chem.*, 1907, [ii], 76, 93—97. Compare Abstr., 1906, i, 901).—*Phenylglyoxalidone*, $C_9H_8ON_2$, is formed by the interaction of glycine ethyl ester and benziminoethyl ether. It is oxidised in acetic acid solution by atmospheric oxygen with the formation of a red substance, probably identical with glyoxaline-red (Ruhemann and Stapleton, Trans., 1900, 77, 804).

Methylglyoxalidone, 
$CMe\Big<\genfrac{}{}{0pt}{}{N—CO}{NH{\cdot}CH_2}$ or 
$CMe\Big<\genfrac{}{}{0pt}{}{N—C{\cdot}OH}{NH{\cdot}CH}$, is formed when acetiminoethyl ether and glycine ethyl ester are mixed in molecular proportions; it forms white crystals, m. p. 140—141°, is decomposed on boiling with alkalis, and combines in alkaline solution with diazonium compounds with the formation of azo-dyes.

The *hydrochloride*, $C_4H_6ON_2,HCl$, crystallises in small, brown needles.

The *compound*, 
$CMe\Big<\genfrac{}{}{0pt}{}{N—CH{\cdot}CH—N}{NBz{\cdot}CO\ \ CO{\cdot}NH}\Big>CMe$, glistening, white leaflets, m. p. 216—218° (decomp.), is obtained by the benzoylation of methylglyoxalidone by the Schotten-Baumann method. The action of benzoyl chloride on the base in pyridine solution leads to the formation

of *methylglyoxalidone dibenzoate*, $C_{18}H_{14}O_3N_2$, crystallising in small, slender, white needles, m. p. 128°. The *dibenzylidene* derivative,

$$CHPh{:}CH\cdot C<\begin{matrix}N\text{---}C{:}CHPh\\ NH\cdot CO\end{matrix}$$

, m. p. 218°, is prepared by heating methylglyoxalidone with an excess of benzaldehyde, or by shaking an alkaline solution of the base with benzaldehyde.

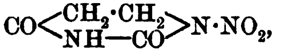
Attempts to prepare *N*-alkylglyoxalidones by employing sarcosine ethers in place of glycine ethyl ester were unsuccessful.

Monochloroacetiminoethyl ether, C_4H_8ONCl, prepared by Pinner's method, is a liquid which decomposes when boiled under atmospheric pressure; it has a pyridine-like odour and produces inflammation of the mucous membrane. W. H. G.

Action of Concentrated Nitric Acid on Trimethyleneureine and on Hydrouracil.

Antoine P. N. Franchimont and Hermann Friedmann (*Rec. trav. chim.*, 1907, **26**, 218—222).—Donk (this vol., i, 831) finds that the action of nitric acid on glycine anhydride does not conform to the law laid down by Franchimont (Abstr., 1889, 1145) concerning the action of concentrated nitric acid on cyclic derivatives containing a NH group situated between the carbonyl group and the residue of a saturated hydrocarbon. The law is supported by the course of the action of nitric acid on trimethyleneureine and on hydrouracil.

Nitrohydrouracil,

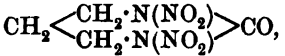


$$CO<\begin{matrix}CH_2\cdot CH_2\\ NH\text{---}CO\end{matrix}>N\cdot NO_2$$

, prepared by dissolving hydrouracil in concentrated nitric acid, is deposited from ethyl acetate in shining crystals, decomposing at 155—158°, and dissolves readily in water or methyl alcohol and sparingly in ether, light petroleum, benzene, chloroform, or carbon tetrachloride. When boiled with water, nitrohydrouracil (1 mol.) yields carbon dioxide (1 mol.) and *β-nitroaminopropionamide*, $NO_2\cdot NH\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, which separates from water or alcohol in large, colourless crystals, m. p. 122°.

β-Nitroaminopropionic acid, $NO_2\cdot NH\cdot CH_2\cdot CH_2\cdot CO_2H$, prepared by the action of sodium hydroxide solution on the corresponding amide, crystallises from alcohol in long needles, m. p. 73°, and is readily soluble in ether. The formulæ of the *barium*, $C_3H_4O_4N_2Ba,H_2O$, and *silver* salts, $C_3H_4O_4N_2Ag_2$, show that the acid behaves as a dibasic acid.

Dinitrotrimethyleneureine,

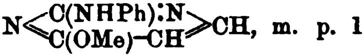
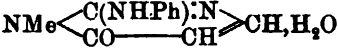
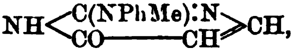


$$CH_2<\begin{matrix}CH_2\cdot N(NO_2)\\ CH_2\cdot N(NO_2)\end{matrix}>CO$$

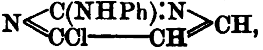
, prepared by the action of concentrated nitric acid on trimethyleneureine, crystallises from alcohol in whitish-yellow needles and yields carbon dioxide and trimethylenedinitroamine when boiled with water. T. H. P.

Pyrimidines. XXI. Action of Methyl Iodide on 6-Oxy-2-anilinopyrimidine and Synthesis of 2-Anilinopyrimidine.

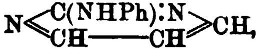
Treat B. Johnson and Frederick W. Heyl (*Amer. Chem. J.*, 1907, **38**, 237—249).—It has been shown previously (this vol., i, 728) that by the action of methyl iodide or ethyl iodide on 6-oxy-2-ethylthiolpyrimidine in presence of alkali hydroxide, the corresponding 1-alkyl derivatives are produced, but neither the corresponding oxygen ethers nor the 3-alkyl derivatives are formed. The action of methyl iodide on 6-oxy-2-anilinopyrimidine (Johnson and Johns, Abstr., 1906, i, 456) in presence of potassium hydroxide has now been studied, and it is found that a mixture of 2-anilino-6-methoxypyrimidine and 6-oxy-2-anilino-1-methylpyrimidine is produced.

2-*Anilino*-6-*methoxypyrimidine*,  $\mathrm{N}\left<\begin{matrix}\mathrm{C(NHPh){:}N}\\ \mathrm{C(OMe){-}CH}\end{matrix}\right>\mathrm{CH}$, m. p. 119°, best prepared by the action of methyl iodide on the silver derivative of 6-oxy-2-anilinopyrimidine, forms transparent prisms. 6-*Oxy*-2-*anilino*-1-*methylpyrimidine*,  $\mathrm{NMe}\left<\begin{matrix}\mathrm{C(NHPh){:}N}\\ \mathrm{CO{-\!-\!-}CH}\end{matrix}\right>\mathrm{CH,H_2O}$, m. p. 149—150°, crystallises in slender prisms. This compound can also be obtained by heating 6-oxy-2-ethylthiol-1-methylpyrimidine (Johnson and Heyl, *loc. cit.*) with aniline at 150°. The isomeric 6-*oxy*-2-*methylanilinopyrimidine*,  $\mathrm{NH}\left<\begin{matrix}\mathrm{C(NPhMe){:}N}\\ \mathrm{CO{-\!-\!-}CH}\end{matrix}\right>\mathrm{CH}$, m. p. 187°, obtained by heating 6-oxy-2-ethylthiolpyrimidine with methylaniline, forms large, prismatic crystals.

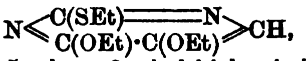
6-Oxy-2-anilinopyrimidine reacts smoothly with phosphorus oxychloride with formation of 6-*chloro*-2-*anilinopyrimidine*,


$$\mathrm{N}\left<\begin{matrix}\mathrm{C(NHPh){:}N}\\ \mathrm{CCl{-\!-\!-}CH}\end{matrix}\right>\mathrm{CH},$$

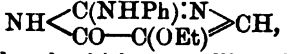
m. p. 134°, which crystallises in plates. When this substance is digested with water and zinc dust, 2-*anilinopyrimidine*,

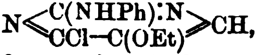

$$\mathrm{N}\left<\begin{matrix}\mathrm{C(NHPh){:}N}\\ \mathrm{CH{-\!-\!-}CH}\end{matrix}\right>\mathrm{CH},$$

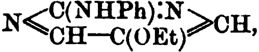
m. p. 116°, is produced, which forms prismatic crystals; its *hydrochloride*, decomp. 125°, *sulphate*, m. p. 140—142°, and *platinichloride*, m. p. 218—221° (decomp.), are described. Attempts to hydrolyse 2-anilinopyrimidine and 6-oxy-2-anilinopyrimidine with formation of 2-oxypyrimidine and uracil respectively were unsuccessful. Carbon disulphide does not react with these pyrimidines.

5:6-*Diethoxy*-2-*ethylthiolpyrimidine*,  $\mathrm{N}\left<\begin{matrix}\mathrm{C(SEt){=\!=\!=}N}\\ \mathrm{C(OEt){\cdot}C(OEt)}\end{matrix}\right>\mathrm{CH}$, was obtained as an oil by treating 6-chloro-5-ethoxy-2-ethylthiolpyrimidine (Johnson and McCollum, Abstr., 1906, i, 704) with sodium ethoxide; its *hydrochloride*, m. p. 129—131°, forms prismatic crystals.

6-Oxy-5-ethoxy-2-methylthiolpyrimidine is not changed by the action of alcoholic ammonia at 140—160° or at 210—235°. When 6-oxy-5-ethoxy-2-ethylthiolpyrimidine is heated with aniline at 185—216° for two hours, 6-*oxy*-2-*anilino*-5-*ethoxypyrimidine*,

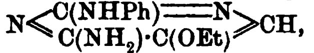

$$\mathrm{NH}\left<\begin{matrix}\mathrm{C(NHPh){:}N}\\ \mathrm{CO{-}C(OEt)}\end{matrix}\right>\mathrm{CH},$$

m. p. 231—232°, is produced, which crystallises in plates and, when warmed with phosphorus oxychloride, is converted into 6-*chloro*-2-*anilino*-5-*ethoxypyrimidine*,  $\mathrm{N}\left<\begin{matrix}\mathrm{C(NHPh){:}N}\\ \mathrm{CCl{-}C(OEt)}\end{matrix}\right>\mathrm{CH}$, m. p. 111—112°, which forms stout prisms. On treating the last-mentioned compound with zinc dust and water, 2-*anilino*-5-*ethoxypyrimidine*,


$$\mathrm{N}\left<\begin{matrix}\mathrm{C(NHPh){:}N}\\ \mathrm{CH{-}C(OEt)}\end{matrix}\right>\mathrm{CH},$$

m. p. 130—131°, is obtained, and crystallises in short prisms.

When 6-chloro-2-anilino-5-ethoxypyrimidine is heated with alcoholic ammonia at 180—188°, 6-*amino-5-ethoxy-2-anilinopyrimidine*,

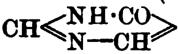


$$N<\begin{array}{l}C(NHPh)=\!=\!=N\\C(NH_2)\cdot C(OEt)\end{array}>CH,$$

m. p. 133—134°, is formed, and crystallises in prisms. E. G.

Pyrimidines. XXII. Salts of Cytosine, *iso*Cytosine, 6-Aminopyrimidine, and 6-Oxypyrimidine. HENRY L. WHEELER (*J. Biol. Chem.*, 1907, 3, 285—297).

—6-*Oxypyrimidine*, CH<NH·CO / N—CH>CH, is



$$CH<\begin{array}{l}NH\cdot CO\\N-CH\end{array}>CH$$

formed by the action of hydrogen peroxide on 2-thiouracil (Wheeler and Bristol, Abstr., 1905, i, 483) or, better, by the action of hydriodic acid and red phosphorus on 2 : 6-dichloropyrimidine. It crystallises from benzene or ethyl acetate in colourless needles, m. p. 164—165°, and, unlike uracil (dioxypyrimidine), gives no coloration with bromine and barium hydroxide. The *acetyl* derivative, $C_6H_8O_3N_2$, forms colourless needles melting at 180° to a clear oil, which then solidifies and subsequently melts and decomposes at 215—220°, and is probably acetylformamidine-acrylic acid. The *picrate*, $C_{10}H_7O_8N_5$, forms flat crystals, m. p. 190°, and is more readily soluble than the picrates of cytosine and *iso*cytosine. The *hydrochloride*, $C_4H_4ON_2,HCl,H_2O$, is readily soluble, and crystallises in thick, transparent prisms which melt partially at 100° and completely at 205—210°. The *sulphate*, $(C_4H_4ON_2)_2,H_2SO_4$, m. p. 218° (decomp.), is also readily soluble.

6-Aminopyrimidine (Büttner, Abstr., 1903, i, 658) is readily obtained by reducing 2-chloro-6-aminopyrimidine with hydriodic acid and red phosphorus. The *acetyl* derivative, $C_6H_7ON_3$, crystallises from water in slender needles, m. p. 202°. The *picrate*, $C_{10}H_8O_7N_6$, forms bright yellow, slender needles, m. p. 226°. The *hydrochloride*, $C_4H_5N_3,HCl$, forms transparent prisms or plates, m. p. 257°. *Cytosine hydrochloride*, $C_4H_5ON_3,HCl,H_2O$, is obtained when the normal chloride (Wheeler and Johnson, Abstr., 1903, i, 526) is recrystallised from water. It loses its water at 50° and then melts at 275—279°.

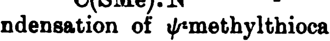
An iso*cytosine hydrochloride*, $C_4H_5ON_3,HCl$, m. p. 270° (decomp.), and *sulphate*, $(C_4H_5ON_3)_2,H_2SO_4$, m. p. 276° (decomp.), have been prepared. Cytosine forms a normal sulphate, $(C_4H_5ON_3)_2,H_2SO_4,2H_2O$ (Levene, Abstr., 1903, i, 668), a basic sulphate,

$$(C_4H_5ON_3)_4,H_2SO_4,2H_2O,$$

and an acid sulphate, $C_4H_5ON_3,H_2SO_4$, m. p. 197° (Kossel and Steudel, Abstr., 1903, i, 667). J. J. S.

Pyrimidines. Synthesis of Thymine-4-carboxylic Acid. TREAT B. JOHNSON (*J. Biol. Chem.*, 1907, 3, 299—306).

—6-*Oxy-2-methylthiol-5-methylpyrimidine-4-carboxylic acid*,

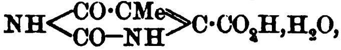


$$NH<\begin{array}{l}CO-CMe\\C(SMe):N\end{array}>C\cdot CO_2H,$$

is formed by the condensation of ψ-methylthiocarbamide hydriodide and ethyl sodio-oxalylpropionate in the presence of potassium hydroxide solution (2 equiv.). It crystallises from hot water or alcohol, in both of which it is sparingly soluble, in prisms, m. p. 243—244° (decomp.).

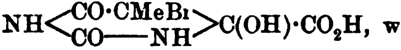
When 1 equiv. of potassium hydroxide is used in the condensation, the product is the *ethyl* ester, $C_9H_{12}O_3N_2S$, of the above acid. It crystallises in slender needles, m. p. 201—202°. The *potassium* salt, $C_7H_7O_3N_2SK,6H_2O$, crystallises from hot water in needles, decomp. 230°. When heated in a sulphuric acid bath at 245° until effervescence is completed, it yields 6-oxy-2-methylthiol-5-methylpyrimidine.

A quantitative yield of *thymine-4-carboxylic acid*,



$$NH<\begin{matrix}CO\cdot CMe\\CO-NH\end{matrix}>C\cdot CO_2H,H_2O,$$

is obtained when the pyrimidine-carboxylic acid is digested with concentrated hydrochloric acid. It crystallises from water in an anhydrous state, and also with $1H_2O$, but both forms decompose at 328—330°. The acid is not affected by treatment at 160—170° with 20% sulphuric acid, and hence thymine cannot exist in nucleic acids as a 4-carboxylic derivative. *Potassium*, *barium*, and *lead* salts have been prepared. The *ethyl* ester, $C_8H_{10}O_4N_2$, crystallises from water in distorted prisms, m. p. 255°. Bromine and water convert the acid into 5-*bromo*-4-*hydroxy*-5-*methyl*-4 : 5-*dihydrothymine*-4-*carboxylic acid*,



$NH<\begin{matrix}CO\cdot CMeBr\\CO—NH\end{matrix}>C(OH)\cdot CO_2H$, which crystallises in small prisms decomposing rapidly at 295—300°. J. J. S.

2 : 3-Naphthylenedihydrazine. HARTWIG FRANZEN (*J. pr. Chem.*, 1907, [ii], **76**, 205—232).—If phenols are heated with ammonia, ammonio-zinc chloride, or ammonio-calcium chloride, the hydroxyl groups are replaced by amino-groups. The present work was undertaken to determine the conditions under which the hydroxyls of phenols can be displaced similarly by the hydrazino-group $\cdot NH\cdot NH_2$. Although, according to Hoffmann (Abstr., 1899, i, 221), α- and β-naphthols form the corresponding hydrazines when heated with hydrazine hydrate at 160°, and small amounts of phenylhydrazine are obtained by heating phenol with hydrazine hydrate at 220°, attempts to prepare hydrazines in this manner from polyphenols of the benzene series were unsuccessful. Bucherer and his co-workers have shown that amino-compounds are formed when phenols are heated with ammonium sulphite and ammonia (Abstr., 1903, i, 627 ; 1904, i, 309, 395 ; 1905, i, 48, 585 ; this vol., i, 509) ; it is found now that 1 : 5- and 2 : 3-dihydroxynaphthalenes form the corresponding dihydrazines when heated with hydrazine sulphite and hydrazine hydrate, whilst in the same manner α- and β-naphthols form α- and β-naphthylhydrazines in yields greater than are obtained under Hoffmann's conditions. α- and β-Naphthylhydrazines are formed also when hydrazine α- and β-hydroxynaphthoates are heated slightly above their m. p.'s.

2 : 3-*Naphthylenedihydrazine*, $C_{10}H_6(NH\cdot NH_2)_2$, prepared in a 57% yield by boiling 2 : 3-dihydroxynaphthalene with hydrazine sulphite and hydrazine hydrate in absolute alcoholic solution in a reflux apparatus, or in a 30% yield in the absence of the sulphite, crystallises from benzene in white needles or from alcohol in reddish-brown needles, m. p. 155—156° (decomp.), or from water in reddish-brown needles, m. p. 167—168° (decomp.), or from amyl alcohol in brownish-yellow needles, m. p. 175—176° (decomp.) ; the alcoholic mother-

liquor has a strong blue fluorescence. The dihydrazine readily reduces Fehling's and ammoniacal silver solutions, gives a dark red coloration when treated with mercuric oxide in ethereal solution, or with concentrated sulphuric acid a dark red coloration becoming yellow on dilution, and on treatment with sodium nitrite in hydrochloric or sulphuric acid solution yields a yellow precipitate changing into a dark brown powder. The *hydrochloride*, $C_{10}H_{12}N_4,2HCl$, *sulphate*, $C_{10}H_{12}N_4,H_2SO_4$, decomp. 120°, *picrate*, $C_{10}H_{12}N_4,2C_6H_3O_7N_3$, bronze-yellow leaflets, and *acetate*, $C_{10}H_{12}N_4,2C_2H_4O_2$, m. p. 141—142° (decomp.), are described. When boiled with 15% hydrochloric acid, the dihydrazine is converted into 2:3-naphthyleneazoimide and ammonia, and is reduced to naphthalene when boiled with copper sulphate in aqueous solution. 2:3-Dichloronaphthalene is formed when the dihydrazine is boiled with copper sulphate in hydrochloric acid solution. The *disemicarbazide*, $C_{10}H_6(NH{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$, has m. p. 234—235° (decomp.). The *diphenylthiosemicarbazide*,

$$C_{10}H_6(NH{\cdot}NH{\cdot}CS{\cdot}NHPh)_2,$$

forms brown crystals, m. p. 166° (decomp.). The *diacetyl* derivative, $C_{10}H_6(N_2H_2Ac)_2$, crystallises in white needles, m. p. 231° (decomp.). *Dibenzylidene-2:3-naphthylenedihydrazone*, $C_{10}H_6(NH{\cdot}N{:}CHPh)_2$, crystallises in lemon-yellow needles, m. p. 205° (decomp.), which cannot be obtained quite free from 1:3-*dibenzylideneamino-2-phenyl-2:3-dihydro-ββ-naphthiminazole*; when treated with amyl nitrite, the hydrazone forms a red *substance*, soluble in alcohol, whilst the iminazole remains unchanged. On reduction with zinc dust and glacial acetic acid, the dibenzylidenehydrazone yields 2:3-naphthyleneazoimide. The *di-m-chlorobenzylidene* derivative,

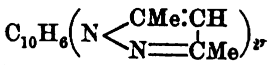
$$C_{10}H_6(NH{\cdot}N{:}CH{\cdot}C_6H_4Cl)_2,$$

crystallises in yellow needles, m. p. 192—193°. The *dipropylidene* derivative, $C_{10}H_6(NH{\cdot}N{:}CMe_2)_2$, crystallises in white needles, m. p. 145—146°, and decomposes gradually when exposed to air. The *diacetophenone* derivative, $C_{10}H_6(NH{\cdot}N{:}CPhMe)_2$, forms brownish-yellow leaflets, m. p. 144°. The *dipyruvic acid* derivative,

$$C_{10}H_6(NH{\cdot}N{:}CMe{\cdot}CO_2H)_2,$$

crystallises in yellow needles, m. p. 180° (decomp.), and dissolves in alkalis forming yellow solutions.

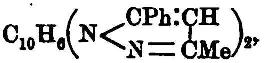
2:3-*Naphthylenedi*-3:5-*dimethylpyrazole*,



$$C_{10}H_6\left(N<\begin{matrix}CMe{:}CH\\ N{=}CMe\end{matrix}\right)_2,$$

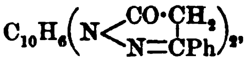
formed with development of heat by the action of acetylacetone on the dihydrazine in alcoholic solution, crystallises in yellow needles, m. p. 126—127°. The *picrate*, $C_{32}H_{26}O_{14}N_{10}$, crystallises in yellow needles, m. p. 187—188°; the *hydrochloride*, $C_{20}H_{20}N_4,2HCl$, is hydrolysed by water; the *dimethiodide*, $C_{22}H_{26}N_4I_2$, crystallises in yellow leaflets, m. p. 225°.

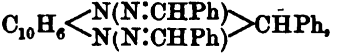
2:3-*Naphthylenedi*-5-*phenyl*-3-*methylpyrazole*,



$$C_{10}H_6\left(N<\begin{matrix}CPh{:}CH\\ N{=}CMe\end{matrix}\right)_2,$$

formed by boiling the dihydrazine with benzoylacetone in alcoholic solution, separates in white crystals, m. p. 191°. The *picrate*, $C_{42}H_{30}O_{14}N_{10}$, crystallises in yellow leaflets, m. p. 200°; the *hydrochloride*, $C_{30}H_{24}N_4,2HCl$, crystallises in white needles.

2 : 3-*Naphthylenedi-3-phenylpyrazolone*,  $C_{10}H_6\left(N{<}\begin{matrix}CO\cdot CH_2\\ N{=}CPh\end{matrix}\right)_2$, prepared by heating 2 : 3-naphthylenedihydrazine with ethyl benzoylacetate, forms a yellowish-brown, crystalline powder, m. p. 245°, and yields a *diisonitroso*-derivative, $C_{28}H_{18}O_4N_6$, crystallising in reddish-brown needles, m. p. 222°.

1 : 3-*Dibenzylideneamino-2-phenyl-2 : 3-dihydro-ββ-naphthiminazole*,  $C_{10}H_6{<}\begin{matrix}N(N{:}CHPh)\\ N(N{:}CHPh)\end{matrix}{>}CHPh$, prepared by boiling 2 : 3-naphthylenedihydrazine with benzaldehyde in alcoholic solution in a reflux apparatus, crystallises from xylene in yellow needles, m. p. 227—228° (decomp.). The corresponding *di-o-hydroxybenzylidene* compound, $C_{31}H_{24}O_3N_4$, is obtained as a lemon-yellow, crystalline powder, m. p. 242° (decomp.). The *di*-m-*chlorobenzylidene* compound, $C_{31}H_{21}N_4Cl_3$, forms a yellow, crystalline powder, m. p. 218°. G. Y.

Behaviour of Diazonium Compounds towards Keto-Enolic Desmotropic Compounds. J. BISHOP TINGLE (*J. Amer. Chem. Soc.*, 1907, **29**, 1242—1243).—The author points out that a number of additive compounds of the type discussed by Dimroth (this vol., i, 662) have been described by himself and his co-workers (compare Abstr., 1906, i, 902), and adds that if Dimroth's reasoning is correct, the problem under consideration may be regarded as having been solved years ago. E. G.

Action of Diazo-salts on Vanillin. ERNESTO PUXEDDU (*Gazzetta*, 1907, **37**, i, 592—595).—The action of diazobenzene chloride on vanillin yields *bisbenzeneazovanillin*, $C_{20}H_{16}O_3N_4$, which crystallises from aqueous alcohol in dark chocolate-coloured, prismatic needles, m. p. 122°, dissolves in dilute alkali solutions giving a blood-red solution which subsequently deposits the unchanged compound, and is readily soluble in organic solvents. With phenylhydrazine, it gives a yellow *compound*, m. p. 178°, which is probably a reduction product. T. H. P.

Oxidising Ferments. [IV.] Specific Nature of Tyrosinase and its Action on the Products of Protein Degradation. ROBERT CHODAT and W. STAUB (*Arch. Sci. Phys. Nat.*, 1907, [iv], **24**, 172—191. Compare this vol., i, 574, 575).—The oxidising action of tyrosinase on tyrosine is diminished by the presence of amino-acids, such as glycine, leucine, or alanine. Tyrosinase acts on dipeptides, such as tyrosine anhydride and glycyltyrosine anhydride, giving rise to a yellow coloration which does not become subsequently red, violet, or black, as in the case of tyrosine. When, however, an amino-acid, such as glycine, leucine, or alanine, is added to the mixture, the red coloration characteristic of tyrosine is obtained. A mixture of glycyltyrosine anhydride with glycine gives a rose colour changing to a bluish-green; it shows a deeper red with alanine and a deep brown with leucine. It is possible with tyrosinase to detect tyrosine in the products of peptolysis, and, with the addition of amino-acids, peptides containing tyrosine can be recognised.

Phenylalanine is not attacked by tyrosinase; the action of this ferment does not therefore depend on the presence of a benzene nucleus in an amino-acid. Tyrosinase acts markedly on *p*-cresol, less strongly on *m*-cresol, and only feebly on *o*-cresol, giving brownish-yellow or yellow solutions. The hydrogen peroxide-peroxydase system (the equivalent of laccase) behaves very differently, forming an insoluble, colourless compound with *p*-cresol, a flesh or dirty-red substance with *m*-cresol, and a deep brown compound with *o*-cresol. Tyrosinase is thus specifically different from laccase; it oxidises the homologues of phenol, in particular, those like tyrosine which have side-chains in the para-position. Millon's reagent is specific for benzene derivatives containing one hydroxyl group; unlike tyrosinase, it acts most vigorously on meta-derivatives.

The action of tyrosinase on *p*-cresol is well suited for its detection and differentiation from laccase. The addition of glycine or other amino-acids much increases the rapidity of the reaction, a violet and finally a blue solution with a red fluorescence being obtained.

E. F. A.

Coagulation of the Proteins by the Action of Ultra-violet Light and of Radium. GEORGES DREYER and OLAV HANSSEN (*Compt. rend.*, 1907, **145**, 234—236).—The action of the light from a Bang lamp on solutions of the natural proteins, serum- and egg-albumin, crystalline globulin, fibrinogen, horse-serum, syntonin, peptone, vegetable vitellin, and caseinogen, has been examined. Serum and egg-albumin and, most of all, globulin are coagulated by the intense and prolonged action of the light, both in alkaline, neutral, and acid solution, but most readily in the latter. A fibrinogen solution remains clear during illumination. Horse-serum is only slightly coagulated, but if previously acidified with acetic acid a very pronounced coagulation results. Syntonin is not coagulated either in acid or alkaline solution. Solutions of peptone and of caseinogen are not coagulated, but acquire a straw-yellow colour. Vitellin coagulates more readily than any other substance studied. Continuous illumination appears to produce a quantitative precipitation. A yellow solution of lecithin is decolorised, but remains clear.

That the phenomenon is a real coagulation and not mere precipitation is shown by the insolubility of the precipitates. It is produced by the ultra-violet rays retained by the glass. When a solution of protein thus acted on is exposed with a large free surface to the action of the light, the surface becomes covered with a protein membrane of thickness varying with the substance.

Vitellin, but not the other proteins, is coagulated by the radiation from radium.

E. H.

Action of Neutral Salts on the Coagulation Temperature of One of the Muscular Proteins. G. BONAMARTINI (*Gazzetta*, 1907, **37**, ii, 190—200).—The author has isolated from ox-muscle a solution of a protein which coagulates at 41—42°, this temperature being influenced neither by the salts naturally accompanying the protein nor by a change in the concentration from 1 muscle : 5 water to 1 muscle : 20 water. The influence of sodium chloride, ammonium chloride and sulphate, and magnesium sulphate in lowering the temperature of coagulation of the protein was studied, the results being given in the form of curves and tables. At definite concentrations, the various salts produce spontaneous coagulation of the protein at the ordinary temperature. The coagulation of the protein under the influence of larger or smaller proportions of salts probably yields a mixture of coagulated with precipitated protein in some cases, and precipitated protein only in others. Indeed, the coagulum obtained by means of ammonium chloride or sulphate at 14·5° re-dissolves completely in water, and all the coagulums obtained at temperatures lower than that of true coagulation are more or less soluble in water.

T. H. P.

Fractionation of Agglutinins and Antitoxin. Robert B. Gibson and Katharine R. Collins (*J. Biol. Chem.*, 1907, **3**, 233—251); Edwin J. Banzhaf and Robert B. Gibson (*ibid.*, 253—264).—Researches of others, and the present investigations, show the untrustworthiness of any differentiation of antitoxins, &c., as contained in the various protein fractions separable by salting-out (pseudoglobulin, euglobulin, &c.). The same is true for agglutinins.

The globulin obtained by saturation of serum with sodium chloride is more potent in antitoxin per gram of protein than the fractions precipitated by lower concentrations of ammonium sulphate, and it is practicable by such a method to prepare a solution of high antitoxic value from relatively weak plasma. W. D. H.

Hydrolysis of Nucleoproteins. E. Carapelle (*Centr. Bakt. Par.*, 1907, i, **44**, 440—441).—The nucleoprotein obtained from *Bacillus prodigiosus*, grown on large Petri dishes, by extraction with dilute sodium carbonate and precipitation with acetic acid, was hydrolysed with sulphuric acid, the solution neutralised, and evaporated to dryness. The alcoholic extract of the residue gave a syrup which, when dissolved in water, was dextrorotatory, reduced Fehling's solution and ammoniacal silver nitrate, and formed a yellow phenylosazone, m. p. 185°, after crystallisation from xylene. E. F. A.

Koilin. K. B. Hofmann and Fritz Pregl (*Zeitsch. physiol. Chem.*, 1907, **52**, 448—471).—The horny material constituting the cuticle of the birds' stomach is termed *koilin*. This substance does not belong to the keratins, as the cystin group is either entirely absent or present in only minute quantities. It cannot be grouped with the *membrana testacea* of the hen.

The *membrana testacea* does not consist of keratin, and the name ovokeratin should not be used for this material, and neither it nor koilin can be grouped with any of the ordinary sub-groups of the proteins.

J. J. S.

Organic Chemistry.

Preparation of Tetranitromethane. Conrad Claessen (D.R.-P. 184229).—The production of tetranitromethane from nitroform, which is itself obtained with difficulty from explosive substances such as mercury fulminate, is too dangerous to admit of this process being employed on a large scale. It is now found that the aromatic hydrocarbons and their nitro-derivatives when warmed with a mixture of nitric-sulphuric acid (40% H_2SO_4, 60% HNO_3) and fuming sulphuric acid (50% SO_3) furnish a large amount of tetranitromethane; a yield of 50% on the weight of the organic substance being sometimes obtained. Nitrobenzene when gradually heated with excess of the acid mixture to 120° is decomposed, giving rise to tetranitromethane and a large amount of nitrous fumes. G. T. M.

Improved Method for the Preparation of Alkyl Chlorides. William M. Dehn and Grant T. Davis (*J. Amer. Chem. Soc.*, 1907, **29**, 1328—1334).—A method is described for the preparation of alkyl chlorides by the action of phosphorus trichloride on alcohols in presence of zinc chloride. Propyl chloride has been obtained in a yield amounting to 94% of the theoretical by the use of anhydrous zinc chloride. It has been found that, if a solution of zinc chloride (b. p. 150—160°) is used instead of the anhydrous salt, the yield of propyl chloride is decreased, but that in the case of *iso*butyl and *iso*amyl chlorides larger yields (85% and 88% respectively) are produced. The reaction takes place in accordance with the equation: $6ROH + 2PCl_3 + ZnCl_2 = Zn(H_2PO_3)_2 + 6RCl + 2HCl$. Evidence has been obtained, however, of the formation of complex intermediate products.

By the action of stannic chloride on propyl alcohol, an additive *compound*, b. p. 148°, is obtained. E. G.

Constitution of Methazonic Acid. Wilhelm Meister (*Ber.*, 1907, **40**, 3435—3449. Compare Dunst[illegible] and Goulding, Trans., 1900, **77**, 1262; Scholl, Abstr., 1901, i, 359).—Methazonic acid behaves as a primary nitro-compound, since it gives the nitrolic acid reaction and Konowaloff's reaction, and hence contains the grouping $\cdot CH_2\cdot NO_2$. It reacts with primary aromatic amines and hydrazines, yielding products which also contain the primary nitro-group. These products are formed by the replacement of NHO by :NR, and hydroxylamine is also formed. The reactions are most readily explained by the presence of the oximino-group in methazonic acid, and the formula thus arrived at is $NO_2\cdot CH_2\cdot CH:N\cdot OH$. When the condensation products are reduced, ammonia is formed,

$$NO_2\cdot CH_2\cdot CH:NR \longrightarrow NH_3 + CH_3\cdot CH:NR,$$

and the residue, when distilled with acid, yields an amine and acetaldehyde, $CH_3\cdot CH{:}NR + H_2O \longrightarrow CH_3\cdot CHO + NH_2R$. They closely resemble Schiff's bases.

An *iso*nitro-formula, *β-isonitroacetaldoxime*,

$$OH\cdot NO{:}CH\cdot CH{:}N\cdot OH,$$

is also possible. The formation and reactions of methazonic acid are discussed from the point of view of the new formula.

Attempts have been made to synthesise methazonic acid from β-chloro- or β-iodo-acetaldoxime and silver nitrite, but without success.

Methazonic acid and phenylhydrazine in the presence of hydrochloric acid yield *β-nitroacetaldehyde-phenylhydrazone*,

$$NO_2\cdot CH_2\cdot CH{:}N_2HPh.$$

It may be crystallised in small amounts (0·1—0·2 gram) from light petroleum and forms glistening, white plates, m. p. 74—74·5°. When kept in closed vessels, it rapidly decomposes, but can be kept at 0° in open vessels if protected from sunlight. It dissolves in alkalis, gives the nitrolic acid reaction, and yields precipitates with the salts of the heavy metals.

Nitroacetaldehyde-p-*nitrophenylhydrazone*,

$$NO_2\cdot CH_2\cdot CH{:}N_2H\cdot C_6H_4\cdot NO_2,$$

forms orange-brown flakes which decompose at 141—142°.

β-Nitroethylidene-p-*chloroanil*, $NO_2\cdot CH_2\cdot CH{:}N\cdot C_6H_4Cl$, obtained from the acid and *p*-chloroaniline, crystallises from light petroleum in minute, canary-yellow needles decomposing at about 165°. The corresponding p-*nitroanil*, $NO_2\cdot CH_2\cdot CH{:}N\cdot C_6H_4\cdot NO_2$, crystallises from chloroform in shimmering, yellow needles which decompose at about 183°.

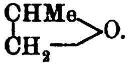
β-Nitroethylideneanil, $NO_2\cdot CH_2\cdot CH{:}NPh$, forms golden-yellow needles, m. p. 94—95° after sintering at 90°.

When hydrolysed with alkali, the *p*-chloroanil yields *p*-chloroaniline, ammonia, hydrogen cyanide, formic acid, methazonic acid, and carbon dioxide. With acids, the same compound yields the same products with the exception of ammonia and methazonic acid, hydroxylamine being formed in place of ammonia. J. J. S.

The Series Resulting from the Methylation of Ethyl Alcohol, with Regard to the Aptitude for Isomeric Change of the Halide Ethe[illegible] —Louis Henry (*Compt. rend.*, 1907, **145**, 547—549).—A comparison is given of the facility with which the halide ethers derived from the ethyl halides, $CH_3\cdot CH_2X$, by replacement (1) in the $\cdot CH_3$ group exclusively; (2) in the $\cdot CH_2X$ group exclusively, and (3) in the $\cdot CH_3$ and $\cdot CH_2X$ group simultaneously of hydrogen by methyl, undergo isomeric change. (1) The normal propyl derivatives change into the *iso*compounds, the *iso*butyl more readily into the tertiary butyl, and the trimethylethyl halides still more readily into the tertiary amyl derivatives. (2) The *iso*propyl and *tert.*-butyl halides do not change isomerically. (3) The secondary butyl halides are stable, but the methyl*iso*propyl carbinol and the methyl *tert.*-butyl carbinol halide ethers are easily transformed into tertiary halide derivatives. The tertiary halide compounds are stable. This review reveals the fact that isomeric change occurs the more readily the less the number of hydrogen atoms combined with the carbon atom attached to the halide-ether chain. Thus the abundant presence of hydrogen confers stability on the polycarbon chains.

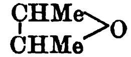
E. H.

Beeswax. II. Psyllostearyl Alcohol as a Constituent. ERNST EDW. SUNDWIK (*Zeitsch. physiol. Chem.*, 1907, **53**, 365—369. Compare Abstr., 1898, i, 617; 1901, i, 358).—By the use of improved methods, the surmise that psyllostearyl alcohol is present in beeswax was confirmed. The wax of *Bombus terrestris* was used in the present instance, acetone being used as the extracting agent. W. D. H.

Propylene Oxide,  $\begin{matrix}CHMe\\|\\CH_2\end{matrix}\!\!>O$. LOUIS HENRY (*Compt. rend.*, 1907, **145**, 453—456).—The action of magnesium ethyl bromide on propylene oxide has been studied in order to ascertain whether it gives rise to a product by simple addition as in the case of ethylene oxide (this vol., i, 745), or whether isomeric change initially occurs as with *s*-dimethylethylene oxide (this vol., i, 817) and *as*-dimethylethylene oxide (this vol., i, 744). The product actually obtained was methyl-*n*-propylcarbinol, $CHMePr^{a}\cdot OH$, which was identified by means of the semicarbazone (m. p. 100°) of the ketone, $COMePr^{a}$, formed on oxidation. The behaviour of propylene oxide is thus similar to that of ethylene oxide; the substitution of a single methyl group is not sufficient to bring about the possibility of undergoing isomeric change which exists in the dimethylated derivatives. It is to be observed that epichlorohydrin on combining with magnesium ethyl bromide gives α-chloro-γ-hydroxy-β-ethylpropane,

$CH_2Cl\cdot CHEt\cdot CH_2\cdot OH$. W. A. D.

Bisecondary Butylene Monochlorohydrin,
$OH\cdot CHMe\cdot CHMeCl$.

LOUIS HENRY (*Compt. rend.*, 1907, **145**, 498—499).—*Bisecondary butylene monochlorohydrin* (γ-*chloro*-sec.-*butyl alcohol*) is prepared by the addition of hypochlorous acid to *s*.-dimethylethylene obtained by the action of alcoholic potash on *sec*.-butyl iodide, CHMeEtI; it is a colourless, somewhat viscous liquid, soluble in about 15 vols. of water at 20°, D^{20} 1·105, μ 1·44376, mol. refraction 26·05 (calc. 26·98), b. p. 138—139°/753 mm. It is very sensitive to alkalis and alkali carbonates, being converted into *s*-dimethylethylene oxide,  $\begin{matrix}CHMe\\|\\CHMe\end{matrix}\!\!>O$ (b. p. 56°). W. A. D.

Crystalline Iron Methoxides. KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1907, **40**, 3764—3766).—*Dimethoxyferric formate*,
$H\cdot CO_2\cdot Fe(OMe)_2$,
and *dimethoxyferric acetate*, $Me\cdot CO_2\cdot Fe(OMe)_2$, are obtained by dissolving iron wire in formic or acetic acid, evaporating the solution, and treating the residue with methyl alcohol in an atmosphere of carbon dioxide; both form yellow, double-refracting crystals, yield formaldehyde in contact with a glowing copper spiral, and decompose

gradually in contact with water and immediately with hydrochloric acid, the solution showing the reactions of a ferric salt.

The formation of these compounds depends on the esterification of the basic ferric salts formed intermediately (compare Hofmann and Höchtlen, Abstr., 1905, i, 38).

The *substance*, $(MeCO_2)_2Fe{\cdot}OEt$, is a red powder, which is obtained by the evaporation in a vacuum of an ethyl-alcoholic solution of ferrous acetate after rapid oxidation in air. C. S.

Some Salts of Glucinum and Zirconium. SEBASTIAN TANATAR and E. KUROBSKI (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 936—943. Compare this vol., i, 261).—The salts obtained by the action of organic acids on glucinum carbonate mostly correspond with the formula Gl_4OX_6. They are non-volatile, but most are soluble in benzene, some also in other organic solvents and in water. In the liquid state they are non-conductors of electricity. The following salts are described. *Formate* [the *compound* $Gl(CHO_2)_2$ was also obtained], *crotonate*, iso*crotonate*, *lævulate*, and *propionate*. Glucinum also forms compounds of the type $Gl_4OX_2X_4'$ and $Gl_4OX_3X_3'$; thus, by heating glucinum butyrate with acetyl chloride, the *compound* $Gl_4O(C_4H_7O_2)_4(C_2H_3O_2)_2$ is obtained as a viscous liquid solidifying at −15°, b. p. 351°. Similarly, the *compound* $Gl_4O(C_3H_5O_2)_3(C_2H_3O_2)_3$ was obtained as a crystalline substance, m. p. 127°, b. p. 330°. The normal salts of glucinum with dibasic acids can be obtained quite readily; the following are described: *succinate*, *citraconate*, maleate, and fumarate. The salts of glucinum are very similar in constitution and solubility to the corresponding zirconium salts. Zirconium *propionate*, iso*butyrate*, *crotonate*, and *succinate* are described. The quadrivalency of glucinum is again insisted on; thus the compounds formed by the metals of the fourth group with acetylacetone are analogous in properties to the corresponding glucinum compound, whereas the compounds of the metals of the second group are quite different. Z. K.

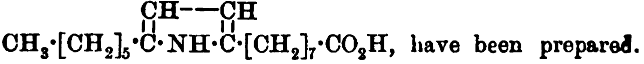
Preparation of Double Lactates containing Antimony. CHEMISCHE FABRIK VON HEYDEN (AKTIEN-GESELLSCHAFT) (D.R.-P. 184202).—Antimonyl sulphate, obtained by the action of sulphuric acid on antimonious sulphide, is introduced into a neutral solution of sodium lactate, the solution is concentrated until the sodium sulphate has separated, and the filtrate then evaporated to dryness. The *sodium antimonyl lactate* thus obtained is a crystalline double salt which dissolves in water without decomposition. *Sodium calcium antimonyl lactate*, a soluble, crystalline, slightly hygroscopic salt, is obtained by partially replacing sodium lactate by the corresponding calcium salt in the foregoing double decomposition.

G. T. M.

Preparation of θκ-Diketostearic Acid. ANDREAS G. GOLDSOBEL (D.R.-P. 180926).—*θκ-Diketostearic acid*,

$$CH_3{\cdot}[CH_2]_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}[CH_2]_7{\cdot}CO_2H.$$

m. p. 96·5°, obtained by oxidising θκ-ketohydroxystearic acid with chromic and acetic acids, was crystallised from water and obtained in white, lustrous leaflets soluble in warm alcohol or benzene. With the exception of its sparingly soluble alkali and ammonium compounds, its salts are insoluble in water. This acid behaves as a δ-diketone, and owing to this circumstance yields derivatives of technical importance. Its *dioxime*, m. p. 113—114°, and its *pyrrole* derivative,

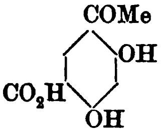


$$\begin{array}{c}CH\text{——}CH\\ \| \qquad \| \\ CH_3\cdot[CH_2]_5\cdot C\cdot NH\cdot C\cdot[CH_2]_7\cdot CO_2H\end{array}$$

have been prepared.

G. T. M.

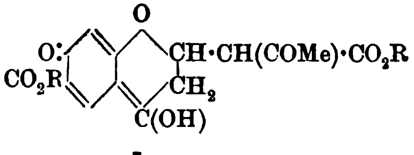
Xanthophanic Acid. II. CARL LIEBERMANN and SIMON LINDENBAUM (*Ber.*, 1907, 40, 3570—3583. Compare Abstr., 1906, i, 556).—The products obtained from xanthophanic acid methyl and ethyl ethers have been further investigated. The acid, m. p. 256° (255°: *loc. cit.*), obtained from the magnesium methoxide "transformation product" of xanthophanic acid methyl or ethyl ether, is shown to be a resacetophenonecarboxylic acid, having probably the annexed structure; the *bromophenylhydrazone* of this, $CO_2H\cdot C_6H_2(OH)_2\cdot CMe\colon N\cdot NH\cdot C_6H_4Br$, crystallises in white needles, m. p. 243°. The acid cannot be esterified by means of alcohol and hydrogen chloride. The *methyl* ester, $C_{10}H_{10}O_5$, formed by the action of methyl iodide on the silver salt, crystallises in colourless needles, m. p. 124—125°, is hydrolysed by boiling alkalis, and when treated with hydrazine hydrate in methyl-alcoholic solution yields a white *hydrazone*, m. p. 174°, solidifying to a yellow *substance*, m. p. above 300°.



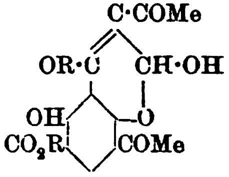
The bromophenylhydrazone, $C_{16}H_{15}O_4N_2Br$, m. p. 224° (*loc. cit.*), has the constitution $CO_2Me\cdot C_6H_2(OH)_2\cdot CMe\colon N\cdot NH\cdot C_6H_4Br$, and is a hydrazone, not of the "transformation product" from which it is prepared, but of methyl resacetophenonecarboxylate; when heated with hydrogen chloride in glacial acetic acid at 125—130°, it yields a mixture of resacetophenonecarboxylic acid and its methyl ester.

The "transformation products," m. p. 162°, obtained by the action of magnesium methoxide on xanthophanic acid methyl and ethyl ethers respectively, are not identical, as they yield different bromides on treatment with hydrogen bromide in benzene solution. The *bromide*, $C_{17}H_{17}O_7Br$, derived from the ethyl ester, crystallises in lemon-yellow needles, m. p. 208° (decomp.), and when shaken with methyl or ethyl alcohol, acetone, or water is hydrolysed, yielding the "transformation product," $C_{17}H_{18}O_8$. The *bromide*, $C_{16}H_{15}O_7Br$, derived from the methyl ester, crystallises in similar needles, m. p. 188° (decomp.), and on hydrolysis yields the "transformation product," $C_{16}H_{16}O_8$.

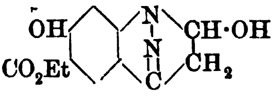
The constitutions of these substances are discussed; it is concluded that the xanthophanic acid ethers have the structure I, and under the influence of magnesium methoxide are transformed into derivatives of the type II. In the transformation of the ethyl ether, a methyl is substituted for the carboxylic ethyl group. The hydroxyl substituted by bromine by the action of hydrogen bromide is that in the heterocyclic nucleus:



I.



II.



When boiled with hydrazine sulphate and sodium acetate in alcoholic solution, xanthophanic acid ethyl ether forms a *hydrazone* crystallising in white needles, m. p. 193—195°, which is considered to have the annexed constitution, and is formed also by the action of semicarbazide on the ethyl ether.

The corresponding *hydrazone*, $C_{11}H_{10}O_4N_2$, derived from the methyl ether, crystallises in needles, m. p. 220°. When heated with fuming hydrochloric acid or hydrogen iodide in acetic anhydride or 10% alkali, these hydrazones yield the *acid*, $C_{10}H_8O_4N_2$, crystallising in yellowish-green needles, m. p. 331—333° (decomp.), and forming solutions with slight blue fluorescence. G. Y.

Glaucophanic Acid. III. CARL LIEBERMANN and H. TRUCHSÄSS (*Ber.*, 1907, 40, 3584—3588. Compare Abstr., 1906, i, 556; and preceding abstract).—Glaucophanic acid methyl and ethyl ethers, which are formed as by-products in the preparation of xanthophanic acid methyl and ethyl ethers respectively, undergo reactions similar to those of the xanthophanic acid ethers, differing only in that the methyl and ethyl ethers yield identical magnesium methoxide "transformation products." In the case of glaucophanic acid ethyl ether, therefore, the action of magnesium methoxide must lead to complete substitution of the ethoxy- by methoxy-groups, whereas only the carboxylic ethoxy-group of xanthophanic acid ethyl ether is substituted. The glaucophanic acid and xanthophanic acid ethers must have a C_{12} nucleus in common, as the action of hydrazine sulphate and sodium acetate on glaucophanic acid ethyl ether leads to the formation of the hydrazone, m. p. 193—195°, obtained from xanthophanic acid ethyl ether.

The magnesium methoxide "transformation product," $C_{20}H_{18}O_9$, is formed from glaucophanic acid methyl ether in a 79% yield; it crystallises in yellow needles, m. p. 217°, and when heated with acetic anhydride and sodium acetate yields a *triacetate*, $C_{20}H_{15}O_9Ac_3$, which crystallises in needles, m. p. 130°, and is hydrolysed to the "transformation product" by cold concentrated sulphuric acid. In presence of a limited amount of acetic anhydride, a yellow *diacetate*, $C_{20}H_{16}O_9Ac_2$, m. p. 166°, is formed. The *bromide*, $C_{20}H_{17}O_8Br$, crystallises in orange-red needles, m. p. 245°, and is stable when dry, but is readily hydrolysed by moist solvents. A *dibromo*-compound, $C_{20}H_{16}O_9Br_2$ or $C_{20}H_{18}O_9Br_2$, formed by the action of bromine on the "transformation product" in carbon disulphide solution, separates from ethyl acetate in crystals, m. p. 225° (decomp.).

The "transformation product" forms a *hydrazone*, $C_{20}H_{20}O_8N_2$, crystallising in white needles, m. p. 217° (decomp.), but when heated with bromophenylhydrazine in boiling methyl-alcoholic solution forms the *bromophenylhydrazone* of a decomposition product, $C_{17}H_{17}O_4N_2Br$, which crystallises in needles, m. p. 161—163° (decomp.), and resembles, but is not identical with, the bromophenylhydrazone obtained from the "transformation product" of xanthophanic acid methyl ether.

The mol. formula of glaucophanic acid ethyl ether, which remains undecided, must lie between C_{23} and C_{27} (compare Claisen, Abstr., 1897, i, 594). G. Y.

Certain Complex Salts of Titanium Peroxide. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 265—273, 349—352; compare this vol., i, 748; ii, 54).—The *compound*,

$$2Na_2C_2O_4,2TiO_3,C_2O_3,4H_2O,$$

prepared by adding excess of hydrogen peroxide to a solution of sodium titano-oxalate and precipitated from solution by the addition of alcohol, is a dense, dark orange, sandy powder, which dissolves readily in water and is extremely hygroscopic in presence of alcohol. It remains unaltered for some time in a dry atmosphere, but in ordinary air it deliquesces, swells, and begins to decompose. The corresponding *potassium* compound, $2K_2C_2O_4,2TiO_3,C_2O_3,2H_2O$, prepared by adding alcoholic potassium acetate solution to alcoholic titanium hydrogen oxalate solution containing hydrogen peroxide, resembles the sodium derivative.

By adding an insufficient amount of barium chloride, together with ammonium acetate, to a solution of sodium titano-oxalate containing the three constituents in the proportions $TiO_2 : 2H_2C_2O_4 : 2Na$ and mixed with hydrogen peroxide, various fractions are precipitated which consist apparently of mixtures of $2BaC_2O_4$, $2TiO_3$, C_2O_3, and BaC_2O_4.

The complexity of the titano-oxalates is shown by the ease with which they can be recrystallised, almost unchanged, from their solutions and by their resistance to hydrolysis by the action of heat. That the degree of complexity is not high is seen from the fact that these salts are decomposed, not only by alkalis, but even by an excess of a barium or calcium salt (compare Rosenheim and Schütte, Abstr., 1901, ii, 244). The alkali pertitano-oxalates, however, are more highly complex, since they are not completely precipitated by ammonia. The introduction of active oxygen into the molecule of titanium oxide is hence, in general, favourable to the formation of complex anions. The statement of Melikoff and Pissarjewsky (Abstr., 1898, ii, 374) that, in the preparation of titanium peroxide, by Classen's method, the clear liquid at first contains an ammonium pertitanate, which decomposes with precipitation of TiO_3,Aq, is probably inaccurate; it is more likely that the TiO_3 is present initially as a complex anion, which is gradually decomposed by the alkali.

The so-called acetate of titanium peroxide (Faber, this vol., ii, 557) is most probably a mixture of peroxide and basic acetate of titanium dioxide. The existence of the phosphate is in accord with the views of the author (*loc. cit.*). T. H. P.

Velocity of the Decomposition of Malonic Acid into Carbon Dioxide and Acetic Acid. JOSEF LINDNER (*Monatsh.*, 1907, **28**, 1041—1047).—The decomposition of malonic acid into carbon dioxide and acetic acid takes place with measurable velocity in glacial acetic acid at 100°. The velocity constant when calculated with the aid of the equation for unimolecular reactions remains satisfactorily uniform throughout the course of the decomposition. The graph formed by plotting the velocity constants determined at 98·5° to 104° against the temperatures is approximately a straight line. G. Y.

Action of α-Chloroacetoacetic Esters on Sodiocyanoacetic Esters. J. CHASSAGNE (*Bull. Soc. chim.*, 1907, [iv], 1, 914—916. Compare Haller and Barthe, Abstr., 1888, 937).—*Ethyl α-cyano-β-acetylsuccinate*, $CO_2Et\cdot CH(CN)\cdot CHAc\cdot CO_2Et$, prepared by the action of ethyl α-chloroacetoacetate on ethyl sodiocyanoacetate, separates from alcohol in crystals, m. p. 83·5—84·5° (corr.), and has the normal molecular weight in freezing acetic acid.

Methyl α-cyano-β-acetylsuccinate, $CO_2Me\cdot CH(CN)\cdot CHAc\cdot CO_2Me$, similarly prepared, separates in crystals, m. p. 89·5—90·5°.

Methyl ethyl α-cyano-β-acetylsuccinate,

$$CO_2Me\cdot CH(CN)\cdot CHAc\cdot CO_2Et,$$

obtained by the interaction of ethyl α-chloroacetylacetate and methyl sodiocyanoacetate, forms crystals, m. p. 93·5—94·5°. The *isomeric* ester, $CO_2Me\cdot CHAc\cdot CH(CN)\cdot CO_2Et$, prepared from methyl α-chloroacetylacetate and ethyl sodiocyanoacetate, has m. p. 88·5—89·5°.

Since these compounds in alcoholic solution give no red coloration with ferric chloride, it is possible that they have an enolic structure. T. H. P.

Conversion of Methyl Alcohol into Formaldehyde. Preparation of Formalin. E. J. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 855—868).—Experiment shows that the ordinarily accepted view of the conversion of methyl alcohol into formaldehyde as well as the ordinary method of preparation are essentially wrong. An elaborate apparatus has been devised which yields satisfactory results for technical purposes. The first stage in the reaction is the catalytic decomposition of methyl alcohol, thus: $MeOH \longrightarrow CH_2O + H_2$. The catalysts employed were freshly reduced copper and asbestos containing precipitated lower oxides of vanadium. The former is the most efficient catalyst, but not more than 60% of the alcohol is ever thus changed. In addition, the formaldehyde decomposes, forming carbon monoxide and hydrogen, which together with carbon dioxide are generally found in the gaseous products. The presence of impurities such as acetone makes no difference in the decomposition of the alcohol. Z. K.

The Effect of Light and Temperature on the Preservation of Formaldehyde Solutions. J. W. de Waal (*Pharm. Weekblad*, 1907, **44**, 1207—1213).—At the ordinary temperature when exposed to light, formaldehyde solutions are not oxidised to formic acid, even in presence of traces of ferric chloride. Rise of temperature promotes the oxidation somewhat, although the effect produced by a temperature of 50° during 400 hours is only slight. A. J. W.

Synthesis of Ketones by aid of Dibromopentane. Julius von Braun (*Ber.*, 1907, **40**, 3943—3948. Compare Perkin and Freer, Trans., 1888, **53**, 202; Perkin and Kipping, *ibid.*, 1890, **57**, 320).—αε-Dibromopentane, ethyl acetoacetate, and sodium react in warm alcoholic solution to form two compounds. *Ethyl* 1-*acetyl*cyclo*hexane carboxylate*, $CO_2Et \cdot C_6H_{10} \cdot COMe$, b. p. 241—245° (decomp.), or 120—124°/11 mm., is a colourless liquid with a piercing aromatic odour, which forms a *semicarbazone*, m. p. 144°, and a p-*nitrophenylhydrazone*, m. p. 145°, and is hydrolysed by aqueous-alcoholic alkali, yielding *cyclo*hexanecarboxylic acid and Darzens' and Bouveault's methyl *cyclo*hexanyl ketone, which has D^{22} 0·893 and forms a reddish-violet p-*nitrophenylhydrazone*, m. p. 154°. The second compound is *ethyl αη-diacetylheptane-αη-dicarboxylate*,

$$CH_3 \cdot CO \cdot CH(CO_2Et) \cdot [CH_2]_5 \cdot CH(CO_2Et) \cdot CO \cdot CH_3,$$

which is very difficultly volatile with steam, and cannot be distilled without decomposing into the *diketone*, $COMe \cdot [CH_2]_7 \cdot COMe$, the formation of which is completed by boiling with alkali. The diketone, m. p. 65°, crystallises in glistening leaflets, and forms a *semicarbazone*, $C_{13}H_{26}O_2N_4$, m. p. 184°, p-*nitrophenylhydrazone*, $C_{23}H_{30}O_4N_6$, m. p. 88°, softening at 85°, and an oxime which yields apparently a mixture of two benzoyl derivatives, of which one has been isolated and has m. p. 90°. C. S.

Isolation of Carbohydrates and Glucosides by Precipitation with Metallic Salts. G. Meillère (*J. Pharm. Chim.*, 1907, **26**, 300—304).—The method of precipitating carbohydrates and glucosides by means of the lead acetates under different conditions is discussed, and attention is drawn to various causes which tend to complicate the fractional precipitation. It is shown that copper acetate may be employed in place of lead acetate for precipitating glucosides, the only difference being that the precipitates are most readily formed in hot solutions. Fractional precipitation may be accomplished by working in acetic acid, neutral, and finally in ammoniacal solutions.

The copper method does not yield good results with many carbohydrates, especially lactose and maltose, as they reduce the copper salt, but may be employed for isolating inositol provided the liquid is neutralised with ammonia. J. J. S.

Action of Cold Aqueous Sodium Hydroxide on Cellulose. Walther Vieweg (*Ber.*, 1907, **40**, 3876—3883).—Wichelhaus and the author (this vol., i, 186) have shown that natural and mercerised cellulose differ from one another in chemical properties. The author now shows the effect of the variation in strength of the sodium hydroxide on cellulose. Experiments are quoted to show the amount of sodium hydroxide taken up by cellulose from alkaline solutions of varying concentration; the conclusion is drawn that a chemical action takes place. The compounds of sodium hydroxide and cellulose are completely decomposed by water, and a product remains which takes up more sodium hydroxide than the original cellulose. Specimens of cellulose were found to differ with respect to the amount of sodium hydroxide which they take up; the "degree of mercerisation" varies from 1 to 3%, and may be estimated by the Schotten-Baumann method. A. McK.

Chemistry and Physiological Action of the Humic Acids. R. A. Robertson, James C. Irvine, and Mildred E. Dobson (*Bio-Chem. J.*, 1907, 2, 458—480).—The natural humic acids prepared from peat differ greatly in composition, and also from the artificial form prepared from sucrose. The acids themselves and their potassium salts serve as organic food for *Penicillium*, both as regards carbon and nitrogen. W. D. H.

Further Observations on the Behaviour of Alkyl Attached to Nitrogen towards Boiling Hydriodic Acid. Guido Goldschmiedt (*Monatsh.*, 1907, 28, 1063—1068. Compare this vol., i, 30; Goldschmiedt and Hönigschmid, Abstr., 1904, ii, 94).—Whilst many substances containing an alkyl group attached to nitrogen have been found when boiled with hydriodic acid to yield the alkyl iodide, with greater or less ease depending on the structure of the nucleus, only negative results have been obtained previously with aliphatic compounds, including tetramethylammonium iodide, benzyldimethylamine, and compounds such as betaine, sarcosine, and methylaminoacetophenone, containing the grouping CO·C·C·NMe, which in the piperidine series yields methyl iodide with special ease. The behaviour towards boiling hydriodic acid of a number of compounds having the group N·Alkyl attached to a tertiary aliphatic carbon has now been investigated, as such substances resemble aromatic compounds in certain respects.

When boiled with hydriodic acid, b. p. 127°, for six hours, and then for a further six hours with hydriodic acid, D 1·9, the following substances yield the percentages quoted of the *N*-alkyl group as the alkyl iodide: 1:2:4:4-tetramethyltrimethyleneimine, 5·4%; 2:4:4-trimethyl-1-ethyl-trimethyleneimine, 2·5%; methyldiacetonealkamine, 7·0%; methylpropyldiacetonealkamine, 20·5%; β-dimethylamino-β-methyl-Δ^{δ}-pentene, 4·4%. On the other hand, α-methylamino-α-phenylbutane-γ-ol, in which the methylamino-group is attached to a secondary carbon atom, does not yield methyl iodide. Since the propyl group must be less reactive than the ethyl group, the high result obtained with methylpropyldiacetonealkamine cannot be ascribed to the formation of propyl iodide.

Whilst the average stability of the methyl groups of a dimethylarylamine is greater than the stability of the methyl of a methylarylamine, the average stability of the methyls of a trimethylarylammonium iodide is much smaller, and the velocity of the formation of methyl iodide correspondingly greater. Thus methylaniline in sixteen and a half hours yields 3·4%, dimethylaniline in eleven and a half hours, 3·9%, and phenyltrimethylammonium iodide in two hours, 6·5% of the total methyl as methyl iodide. Of interest as compared with the behaviour of dimethylaniline is that of tetramethylbenzidine, which in eleven and a half hours yields 7·02% of its methyl as methyl iodide.

When boiled with hydriodic acid, *as*-phenylmethylhydrazine yields 2·93% of the methyl as methyl iodide; at the same time, free iodine is formed in consequence of the reduction of the hydrazine. Which of these is the primary reaction cannot be decided. G. Y.

Bisaquochromium Salts. PAUL PFEIFFER [and, in part, ARMIN TRIESCHMANN, STERN, and PRADE] (*Ber.*, 1907, **40**, 3828—3839).—A number of salts of the diethylenediaminechromium series have been prepared corresponding with the recently described diaquotetra-amminechromium salts (Pfeiffer, this vol., ii, 694). In each case, however, it is found that the diethylenediamine salt contains twice the quantity of water not removed in a desiccator which is present in the corresponding diethylenediamine compound; consequently it is necessary to assume that the single water molecules in the metal complex of the diammine salt are replaced by O_2H_4 molecules in the diethylenediamine compound. The author proposes to name such salts containing the O_2H_4 complex, *bisaquo*-salts (compare Werner and Gubser, Abstr., 1906, ii, 452).

cis-*Bromobisaquodiethylenediaminechromium bromide*,

$$[En_2CrBr(O_2H_4)]Br_2,$$

was originally wrongly described as a monoaquo-salt (Abstr., 1905, i, 34). A concentrated solution of the salt yields with potassium iodide the *iodide*, a brilliant, crystalline, red powder; with potassium thiocyanate, the orange cis-*dithiocyanodiethylenediaminechromium thiocyanate*, $[En_2Cr(SCN)_2]SCN$; with ammonium oxalate, the bordeaux-red *double* salt, $[En_2CrC_2O_4][EnCr(C_2O_4)_2]$; with potassium chromithiocyanate, the *hexathiocyanochromic* salt,

$$[En_2Cr(O_2H_4)Br]_3[Cr(SCN)_6]_2,2H_2O,$$

crystallising in brilliant, violet-red, transparent needles, which are decomposed by light. Concentrated nitric acid probably converts the bromide into the *nitrate*: obtained as an orange-red precipitate.

cis-*Hydroxybisaquodiethylenediaminechromium bromide*,

$$[En_2Cr(O_2H_4)OH]Br_2,$$

prepared by the action of pyridine on the bromobisaquo-bromide, forms compact, bordeaux-red crystals. A concentrated solution of the salt gives with silver nitrate a precipitate of silver bromide free from silver hydroxide; with potassium iodide, a red, crystalline precipitate of the *iodide*. Concentrated hydrobromic acid converts the salt into cis-*dibisaquodiethylenediaminechromium bromide*,

$$[En_2Cr(O_2H_4)_2]Br_3,$$

crystallising in small, orange-red, transparent plates. This salt is converted by pyridine into the hydroxybisaquo-bromide and slowly by hydrobromic acid at the ordinary temperature into the bromobisaquo-bromide. A concentrated aqueous solution of the salt yields with solid potassium oxalate, small, brilliant, orange leaflets of the *oxalate.* The salt is converted when heated alone at 100—120°, also when evaporated with hydrobromic acid on a water-bath, into the *anhydrous* form of cis-*dibromodiethylenediaminechromium bromide*, $[\mathrm{En_2CrBr_2}]\mathrm{Br}$. This substance is also obtained, by evaporating a solution of the bromobisaquo-bromide with a drop of hydrobromic acid on a water-bath, in the form of a violet powder. The anhydrous salt is converted by small quantities of water into a *monohydrate*: obtained as a fine crystalline, violet powder. The *iodide* forms glittering, violet leaflets; the *dithionate* forms brilliant bluish-violet needles; the *nitrate* is obtained as a violet powder. W. H. G.

Complex Derivatives of Optically-Active *l*-Propylenediamine. LEO TSCHUGAEFF and W. SOKOLOFF (*Ber.*, 1907, **40**, 3461—3465).—The great increase in optical activity caused by the addition of certain salts to various optically-active compounds, containing hydroxy-groups, has been ascribed by Walden and others to the formation of cyclic complexes. The influence of ring formation on rotation has been investigated by the authors with certain metal derivatives of *l*-propylenediamine, the cyclic nature of metallic derivatives of *dl*-propylenediamine having already been demonstrated by Werner.

l-Propylenediamine, obtained by the resolution of the *dl*-base by *d*-tartaric acid, has b. p. 121°, D_4^{23} 0·8633, $[\alpha]_D$ $-28·04°$, whereas Baumann gives $D_4^{24·3}$ 0·91186 and $[\alpha]_D$ $-20·96°$.

l-*Propylenediamine hydrochloride*, $\mathrm{C_3H_6(NH_2)_2,2HCl}$, has m. p. 240°, D_4^{25} 1·0575, and $[\alpha]_D^{25}$ $-4·04°$ (in aqueous solution, $p = 19·92$).

The platinum compounds studied were prepared by the interaction of platinum *cis*-dichloro-*l*-propylenediamine, $[\mathrm{PtPnCl_2}]$, in aqueous solution at 100° and the calculated amount of the corresponding bases (*l*-propylenediamine, ammonia, ethylenediamine, or trimethylenediamine); the resulting solutions were concentrated and the compounds precipitated by the addition of alcohol or a mixture of ether and alcohol.

The *compound*, *l*-$[\mathrm{PtPn_2}]\mathrm{Cl_2}$ (where $\mathrm{Pn = NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2}$), has $[\alpha]_D^{25}$ $+46·37°$ for p 16·61 and D_4^{25} 1·0958. [Solvent not stated in this and other cases.—ABSTRACTOR.]

The *compound*, *l*-$\left[\mathrm{Pt}^{\mathrm{Pn}}_{\mathrm{2NH_8}}\right]\mathrm{Cl_2}$, has $[\alpha]_D^{25}$ $+$ 25·17° for p 17·47 and D_4^{25} 1·1141.

The *compound*, *l*-$\left[\mathrm{Pt}^{\mathrm{Pn}}_{\mathrm{En}}\right]\mathrm{Cl_2}$, has $[\alpha]_D^{25}$ $+24·07°$ for p 19·08 and D_4^{25} 1·1195.

The *compound*, *l*-$\left[\mathrm{Pt}^{\mathrm{Pn}}_{\mathrm{Tr}}\right]\mathrm{Cl_2}$, has $[\alpha]_{\mathrm{Auer}}^{25}$ $+23·60$ for p 13·09 and D^{23} 1·0747.

The *compound*, *l*-$[\mathrm{PdPn_2}]\mathrm{Cl_2}$, obtained from $\mathrm{K_2PdCl_4}$ and *l*-propylenediamine, has $[\alpha]_D^{25}$ $+79·25°$ for p 17·68 and D_4^{25} 1·0772.

The *compound*, $[\mathrm{NiPn_3}]\mathrm{Cl_2,2H_2O}$, has $[\alpha]_D^{25}$ $+14·13°$ for p 11·04 and D_4^{25} 1·0253.

It will be observed that, although *l*-propylenediamine and its hydrochloride are lævorotatory, the metallic derivatives examined are dextrorotatory.

The influence of the number of propylenediamine molecules in the complex molecule of the platinum derivatives is clearly seen by a comparison of the molecular rotations of these compounds. A. McK.

Isomeric αβ-Dialkylhydroxylamines. I. α-Methyl-β-ethylhydroxylamine. II. β-Methyl-α-ethylhydroxylamine. LAUDER W. JONES (*Amer. Chem. J.*, 1907, **38**, 253—257).—It has been shown previously (Abstr., 1898, i, 174) that when the sodium salt of hydroxyurethane (carbethoxyhydroxamic acid) is treated with methyl iodide, the methyl ether, OEt·CO·NH·OMe, is produced together with αβ-dimethylcarbethoxyhydroxylamine (hydroxymethylurethane methyl ether), $CO_2Et·NMe·OMe$, which on hydrolysis yields αβ-dimethylhydroxylamine. The corresponding ethyl derivatives were obtained in a similar manner.

When hydroxyurethane methyl ether is treated with ethyl iodide in presence of sodium ethoxide, *carbethoxy-α-methyl-β-ethylhydroxylamine* (*hydroxyethylurethane methyl ether*), $CO_2Et·NEt·OMe$, b. p. 165—166°, is produced as a colourless oil which has a peculiar, rather unpleasant odour. If this compound is heated with strong hydrochloric acid, it is converted into *α-methyl-β-ethylhydroxylamine*, NHEt·OMe, b. p. 60—61°, which is a colourless, alkaline liquid, readily soluble in water, and does not reduce silver nitrate; the *hydrochloride*, m. p. 46—47° (approx.), and the *platinichloride*, m. p. 174—175° (decomp.), are described.

Similarly, methyl iodide reacts with hydroxyurethane ethyl ether to form *carbethoxy-β-methyl-α-ethylhydroxylamine* (*hydroxymethylurethane ethyl ether*), $CO_2Et·NMe·OEt$, b. p. 166—167°, which on hydrolysis yields *β-methyl-α-ethylhydroxylamine*, NHMe·OEt, b. p. 65—65·5°, which furnishes a *hydrochloride*, m. p. 74—75°, and a *platinichloride*, m. p. 170—171° (decomp.). E. G.

Preparation of Acylated Aminoalkyl Esters. J. D. RIEDEL (D.R.-P. 181175. Compare Abstr., 1906, i, 631).—This patent deals with the preparation of substances having the general formula $NR^{III}R^{IV}·CH_2·CR^IR^{II}·OR$, where R and R^{IV} are acyl groups and R^I, R^{II}, and R^{III} are alkyl, aryl, or mixed arylalkyl groups. These compounds have useful antipyretic and hypnotic properties.

Methylaminodimethylethylcarbinol, $NHMe·CH_2·CMeEt·OH$, an oil, b. p. 80°/52 mm., was obtained by heating chlorodimethylethylcarbinol with methylamine in 25% alcoholic solution.

Valerylmethylaminodimethylethylcarbinyl valerate,

$$CHMe_2·CH_2·CO·NMe·CH_2·CMeEt·O·CO·CH_2·CHMe_2,$$

b. p. 162°/26 mm., was prepared by the action of valeryl chloride and aqueous sodium hydroxide on the preceding compound.

Methylaminophenyldimethylcarbinol, $NHMe·CH_2·CMePh·OH$, b. p. 136—138°/31 mm., obtained from chlorophenyldimethylcarbinol and methylamine on treatment with benzoyl chloride at 150°, yielded *benzoylmethylaminophenyldimethylcarbinyl benzoate*,

$$NMeBz·CH_2·CMePh·OBz,$$

m. p. 122°. G. T. M.

Hydroxy- and Ethoxy-Derivatives of Normal Primary Butylamine. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 384—397).—δ-*Ethoxybutylamine*, $OEt\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$, b. p. 153—154°/746 mm., D^{20} 0·8640, n_D 1·42751, obtained by reducing γ-ethoxybutyronitrile by Ladenburg's method, is a colourless, mobile liquid of disagreeable odour and piquant taste, and dissolves in water with development of heat, probably forming a hydrate.

Aminoethyl ether, $NH_2\cdot C_2H_4\cdot OEt$, boils at 73° higher than ethyl ether and 89° higher than ethylamine, whilst δ-ethoxybutylamine boils only 62° higher than ethyl butyl ether and 78° higher than normal primary butylamine, so that the influence on volatility of the two components, $-CH_2\cdot NH_2$ and $-CH_2\cdot OEt$, is less marked when they are separated by the system $-CH_2-CH_2-$ than when they are close together.

The fall in boiling point due to the conversion of normal primary butyl alcohol into the corresponding ethyl ether is 25°, and that resulting from the change of δ-hydroxybutylamine into its ethyl ether is 53°. Similarly, the increase in boiling point due to the introduction of the NH_2 group into normal butane is 74°, whilst that due to the introduction of the same group in the δ-position in normal butyl alcohol is 90°. These differences are probably due to mutual action between the $-CH_2\cdot OH$ and $-CH_2\cdot NH_2$ groups being greater than that between the groups $-CH_2\cdot OEt$ and $-CH_2\cdot NH_2$.

The increase of boiling point resulting from the conversion of the normal paraffins into the corresponding primary alcohols is greater than that due to their conversion into the corresponding primary amines, probably because the alcohols are associated. Similarly, the increase in boiling point on passing from alcohols to the corresponding glycols is greater than that observed in changing from monoamines to the corresponding diamines.

The transformation of an amine into the corresponding amino-alcohol is accompanied by a rise of boiling point almost as great as that observed on passing from the hydrocarbon to the corresponding alcohol, and greater than that due to the conversion of the alcohol into the corresponding amino-alcohol, as the following example shows: $CH_3\cdot CH_2\cdot NH_2 \longrightarrow OH\cdot CH_2\cdot CH_2\cdot NH_2 = +152°$. $CH_3\cdot CH_2\cdot OH \longrightarrow NH_2\cdot CH_2\cdot CH_2\cdot OH = +93°$. This difference is probably due, in part, to association in the case of the hydroxy-compounds, and, in part, to mutual action between the $-CH_2\cdot NH_2$ and $-CH_2\cdot OH$ groups.

The increase in boiling point resulting from the change from the simple alcohol to the glycol or from the monoamine to the diamine is less than that due to the conversion of the hydrocarbon into the simple alcohol or monoamine respectively, and as the difference between the increases due to the two changes, hydrocarbon ⟶ alcohol ⟶ glycol, is greater than that exhibited in the case of the two changes, hydrocarbon ⟶ monoamine ⟶ diamine, it may be assumed that the mutual action between two $-CH_2\cdot OH$ groups is greater than that between two $-CH_2\cdot NH_2$ groups. This also explains the fact that a greater difference in volatility is shown between successive members in a homologous series of diamines than between successive members of a homologous series of glycols. The differences observed in the latter series are of the same order as those which obtain in a homologous series of amino-alcohols. The replacement of a $-OH$ group in a glycol by a $-NH_2$ group gives rise at the stages C_2, C_3, and C_4 to the same lowering (24—26°) of the boiling point, and this value is less than that (41—59°) due to the replacement of $-OH$ in a simple alcohol by $-NH_2$. The former case affords a further example of the mutual influence exerted by the groupings $-CH_2\cdot NH_2$ and $-CH_2\cdot OH$. T. A. H.

Diacetoneamine. MORITZ KOHN (*Monatsh.*, 1907, **28**, 1049—1053).—It has been shown previously that the action of magnesium methyl iodide on diacetone alcohol leads to the formation of βδ-dimethylpentane-βδ-diol (Franke and Kohn, Abstr., 1905, i, 111; this vol., i, 171). The action of magnesium methyl iodide on diacetoneamine is found now to lead in the same manner to the formation of β-amino-βδ-dimethylpentane-δ-ol, only a small amount of the diacetoneamine undergoing decomposition into ammonia and mesityl oxide.

β-Amino-βδ-dimethylpentane-δ-ol, $NH_2\cdot CMe_2\cdot CH_2\cdot CMe_2\cdot OH$, is obtained as a mobile oil, b. p. 82°/19—20 mm., has a slight ammoniacal odour, and absorbs carbon dioxide rapidly on exposure to air. The *platinichloride*, $(C_7H_{17}ON)_2,H_2PtCl_6$, crystallises in scarlet, rhombohedric plates; the *picrate*, $C_{13}H_{20}O_8N_4$, forms monoclinic crystals, m. p. 153—155·5°; the *oxalate*, m. p. 212° (decomp.). The action of methyl iodide on β-amino-βδ-dimethylpentane-δ-ol leads to the formation of a *base* which yields an *aurichloride*, $C_{10}H_{23}ON,HAuCl_4$, crystallising in golden leaflets, m. p. 142—143°. *β-Phenylthiocarbamino-βδ-dimethylpentane-δ-ol*, $C_{14}H_{22}ON_2S$, formed by the action of phenylthiocarbimide on β-amino-βδ-dimethylpentane-δ-ol, crystallises in white leaflets, m. p. 115—117°. G. Y.

Cyanogen Bromide as a Means of Testing the Stability of Groups attached to Nitrogen. JULIUS VON BRAUN (*Ber.*, 1907, **40**, 3933—3943).—Previous investigations (Abstr., 1900, i, 430, 641, 687; 1902, i, 365; 1903, i, 464) have shown that the reaction between tertiary bases and cyanogen bromide is represented by $NR^IR^{II}R^{III} + Br\cdot CN = NR^IR^{II}\cdot CN + R^{III}Br$, and that the series allyl, benzyl, methyl, ethyl, propyl, *iso*propyl, and phenyl denotes the increasing order of difficulty with which the group R^{III} is eliminated. Tertiary bases containing the group $\cdot CH_2\cdot CN$ or $\cdot CH_2\cdot CO_2Et$ $(=X)$ react thus: $NR_2X + BrCN \longrightarrow$ (I) $NR_2\cdot CN + BrX$ or (II) $NRX\cdot CN + RBr$. Reaction (I) increases and (II) diminishes as R increases from methyl to butyl.

Biscyanomethylpiperidinium bromide, $C_5NH_{10}(CH_2\cdot CN)_2Br$, obtained from piperidinoacetonitrile and bromoacetonitrile, has m. p. 173° (decomp.); the *platinichloride*, m. p. 192° (decomp.), forms reddish-yellow needles.

Dimethylaminoacetonitrile and cyanogen bromide react energetically to form *cyanomethylaminoacetonitrile*, $CN\cdot NMe\cdot CH_2\cdot CN$, b. p. 150—151°/12 mm., and methyl bromide; the latter reacts with the unchanged dimethylaminoacetonitrile to form *trimethylcyanomethylammonium bromide*, $CN\cdot CH_2\cdot NMe_3Br$, which is readily converted into betaine. The odour of bromoacetonitrile is perceptible only when large quantities of dimethylaminoacetonitrile and cyanogen bromide are reacting.

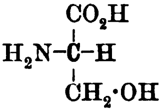
Diethylaminoacetonitrile and cyanogen bromide react to form diethylcyanamide, bromoacetonitrile, *cyanoethylaminoacetonitrile*, $CN\cdot NEt\cdot CH_2\cdot CN$, b. p. 150°/9 mm., and *ethylaminoacetonitrile hydrobromide*, $NHEt\cdot CH_2\cdot CN,HBr$. Ethyl diethylglycine and cyanogen bromide yield diethylcyanamide, ethyl bromoacetate, and *ethyl ethylcyanoglycine*, $CN\cdot NEt\cdot CH_2\cdot CO_2Et$, b. p. 139°.

Dipropylaminoacetonitrile, $NPr^{\alpha}_2\cdot CH_2\cdot CN$, b. p. 89—90°/12 mm., is obtained from dipropylamine by Knoevenagel's method (Abstr., 1904, i, 981); the *methiodide* sinters at 130° and has m. p. 150° (decomp.). It reacts with cyanogen bromide at 100°, and yields dipropylcyanamide, bromoacetonitrile, and 20—25% of *cyanopropylaminoacetonitrile*, $CN\cdot NPr^{\alpha}\cdot CH_2\cdot CN$, b. p. 155—156°/12 mm.

Ethyl dipropylglycine, $NPr^{\alpha}_2\cdot CH_2\cdot CO_2Et$, obtained from dipropylamine and ethyl bromoacetate, has b. p. 204° (decomp.) or 104°/15 mm., and reacts with cyanogen bromide to form probably ethyl bromoacetate, dipropylcyanamide, and ethyl propylcyanoglycine. *Diisobutylaminoacetonitrile*, $N(C_4H_9)_2\cdot CH_2\cdot CN$, b. p. 95—96°/11 mm., requires heating for thirty hours with cyanogen bromide; the products have not been definitely isolated. *α-Diisobutylaminopropionitrile*, $N(C_4H_9)_2\cdot CHMe\cdot CN$, b. p. 101—102°/10 mm., and *α-diisoamylpropionitrile*, $N(C_5H_{11})_2\cdot CHMe\cdot CN$, b. p. 129°/12 mm., react even less favourably with cyanogen bromide. C. S.

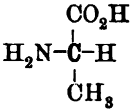
Conversion of *l*-Serine into *d*-Alanine. EMIL FISCHER and KARL RASKE (*Ber.*, 1907, 40, 3717—3724).

—The conversion of *l*-serine into *d*-alanine is effected by treating the hydrochloride of *l*-serine methyl ester with acetyl chloride and phosphorus pentachloride at 0°, whereby the *hydrochloride* of *methyl* 1-*β-chloro-α-aminopropionate*, m. p. 157° (decomp.), is obtained (Fisher and Jacobs, this vol., i, 393), which by hydrolysis with 20% hydrochloric acid at 100° yields the hydrochloride of *l*-*β*-chloro-*α*-aminopropionic acid; the free acid, liberated by lithium or ammonium hydroxide, is reduced to *d*-alanine by sodium amalgam in faintly acid solution. It is highly probable that these reactions are optically normal, and therefore the known configuration of *l*-serine (I) determines that of *d*-alanine (II) and also of *d*-lactic acid (III) obtained from the latter by the action of nitrous acid:



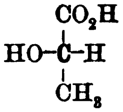
$$\begin{array}{c} CO_2H \\ | \\ H_2N-C-H \\ | \\ CH_2\cdot OH \end{array}$$

I.



$$\begin{array}{c} CO_2H \\ | \\ H_2N-C-H \\ | \\ CH_3 \end{array}$$

II.



$$\begin{array}{c} CO_2H \\ | \\ HO-C-H \\ | \\ CH_3 \end{array}$$

III.

The following constants are given. In aqueous solution, the *hydrochloride* of 1-*β-chloro-α-aminopropionic acid*,

$$CH_2Cl\cdot CH(NH_2,HCl)\cdot CO_2H,$$

has $[\alpha]^{20}_D$ + 0·7°, and the *acid* itself, $[\alpha]^{20}_D$ – 15·46°. r-*β-Chloro-α-aminopropionic acid*, m. p. 160° (decomp.), is reduced to *r*-alanine by sodium amalgam in acid solution; the *hydrochloride*, $CH_2Cl\cdot CH(NH_2,HCl)\cdot CO_2H$, m. p. 172° (decomp.), crystallises in slender needles, and is converted by ammonium hydroxide at 100° into Kleb's hydrochloride of *r*-diaminopropionic acid. The *hydrochloride* of *methyl* r-*β-chloro-a-aminopropionate* has m. p. 134° (decomp.). C. S.

Aminotrimethylacetic [β-Amino-aa-dimethylpropionic] Acid. Moritz Kohn and August Schmidt (*Monatsh.*, 1907, **28**, 1055—1062).—Four of the twelve possible aminovaleric acids have been prepared by Slimmer (Abstr., 1902, i, 206). A fifth isomeride is described in the present paper.

β-Bromo-*aa*-dimethylpropionic acid, m. p. 47° (40·5—41°: Blaise and Marcilly, Abstr., 1904, i, 283), is obtained in a 65—70% yield by treating hydroxypivalic acid at 80° and then at 100° with aqueous hydrogen bromide saturated at 0°. *β-Iodo-aa-dimethylpropionic acid*, $CH_2I\cdot CMe_2\cdot CO_2H$, prepared by boiling hydroxypivalic acid with hydriodic acid, D 1·7, and amorphous phosphorus in a reflux apparatus, crystallises in glistening prisms, m. p. 54°.

β-Amino-aa-dimethylpropionic acid, $NH_2\cdot CH_2\cdot CMe_2\cdot CO_2H$, obtained in a 60% yield by the action of alcoholic ammonia, saturated at 0°, on β-bromo-*aa*-dimethylpropionic acid at the ordinary temperature, crystallises in leaflets, decomp. about 220°, and forms a copper salt crystallising in microscopic, hexagonal plates. The *benzoyl* derivative, $C_5H_{10}O_2NBz$, crystallises in thin needles, m. p. 149—151°. The *phenylcarbamyl* derivative, $C_{12}H_{16}O_3N_2$, crystallises in needles, m. p. 173—175°. The *methylated base* forms a *hydrochloride* as a white, crystalline mass; the *aurichloride*, $C_8H_{16}O_2N,HAuCl_4$, crystallises in needles, m. p. 195—201° (decomp.); the *picrate* crystallises in plates, m. p. 223—225° (decomp.). G. Y.

Polypeptides. XXI. Derivatives of Tyrosine and of Glutamic Acid. Emil Fischer (*Ber.*, 1907, **40**, 3704—3717. Compare this vol., i, 652, 684, 737).—*d*-Alanylglycyl-*l*-tyrosine and *l*-leucyltriglycyl-*l*-tyrosine have been examined in anticipation of the study of the complex derivatives of tyrosine obtained, among other products, by the partial hydrolysis of silk-fibroin. d-*a-Bromopropionylglycyl*-l-*tyrosine*,

$$CHMeBr\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CH_2\cdot C_6H_4\cdot OH)\cdot CO_2H,$$

m. p. 157° (corr.), obtained by the interaction of glycyl-*l*-tyrosine and *d*-*a*-bromopropionyl chloride in cold alkaline solution, separates from water in elongated leaflets, and has in aqueous solution $[a]_D^{20}$ +50·6°. By treatment with 25% ammonium hydroxide for three and a half days at 25°, it is converted into d-*alanylglycyl*-l-*tyrosine*,

$$NH_2\cdot CHMe\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CH_2\cdot C_6H_4\cdot OH)\cdot CO_2H,$$

which froths at 140° and darkens at 180°, responds to Millon's and the biuret reactions, and has $[a]_D^{20}$ +41·9° in aqueous solution. d-*a-Bromo*iso*hexoyltriglycyl*-l-*tyrosine*,

$$C_4H_9\cdot CHBr\cdot CO\cdot [NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(CH_2\cdot C_6H_4\cdot OH)\cdot CO_2H,$$

is prepared from *l*-tyrosine and *d*-*a*-bromo*iso*hexoyldiglycylglycyl chloride in cold alkaline solution; it crystallises in needles, and has $[a]_D^{20}$ +28·7° in aqueous solution. The air-dried substance softens at

100°, and has m. p. 115° (decomp.), whilst the anhydrous compound softens at 100°, gradually darkens, and has m. p. 220°. l-*Leucyltriglycyl*-l-*tyrosine*, $C_{21}H_{31}O_7N_5$, obtained from the preceding compound and 25% ammonium hydroxide at 25°, is a colourless, amorphous substance, which begins to decompose at 160°, and has $[\alpha]_D^{20}$ $+36\cdot5°$ in aqueous solution. It has a bitter taste and an acid reaction, responds to Millon's and the biuret tests, and forms an amorphous *nitrate*, oily *picrate*, and *picrolonate*, and a dark blue *copper* salt. Characteristic of this pentapeptide and of the preceding tripeptide is the property of being precipitated from aqueous solution by ammonium sulphate, a behaviour which recalls that of the albumoses and also of the tetrapeptide obtained by Fischer and Abderhalden (this vol., i, 737) by the partial hydrolysis of silk fibroin.

Glutamic acid is contained in many proteins, but the study of its polypeptides has hitherto been retarded by the difficulty of obtaining crystalline derivatives of the acid. l-*Leucyl*-d-*glutamic acid*,

$$CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H,$$

m. p. 232° (decomp. corr.), obtained by the action of 25% ammonium hydroxide on *d*-*a*-bromo*iso*hexoyl-*d*-glutamic acid, separates from water in long needles, has $[\alpha]_D^{20}$ $+10\cdot5°$ in *N*-hydrochloric acid, is not precipitated from a solution in dilute sulphuric acid by phosphotungstic acid, and forms easily soluble *sodium* and *barium* salts. On the other hand, the *silver* salt is sparingly soluble in water; in virtue of this property, many derivatives of glutamic and also of aspartic acid may be separated from other polypeptides.

The d-*a*-*bromo*iso*hexoyl*-d-*glutamic acid*, m. p. 108—109° (corr.), required in the preceding preparation, is prepared from *d*-glutamic acid and *d*-*a*-bromo*iso*hexoyl chloride in cold alkaline solution.

Triglycylglycinamide,

$$NH_2\cdot CH_2\cdot CO\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

is prepared by heating methyl triglycylglycine for two hours at 80—100° with methyl alcoholic ammonia saturated at 0°. It crystallises in slender needles, sinters and darkens at 225°, and by solution in the dilute acid yields the *nitrate* and the *hydrochloride*; the *picrate* forms orange-red leaflets, and has m. p. 240° (decomp.). Methyl pentaglycylglycine is converted only partially into the amide by liquid ammonia at the ordinary temperature, or by methyl or ethyl alcoholic ammonia at 100°.

The molecular weights of glycyl-*l*-tyrosine, diglycylglycine, triglycylglycine, leucyldiglycylglycine, *l*-alanyldiglycyl-*l*-alanylglycylglycine, and glycyl-*d*-valine anhydride, determined in aqueous solution by the cryoscopic method, are approximately normal.

The acylation of tyrosine leads, as a rule, to the formation of diacyl derivatives; formic acid, however, yields *formyl*-l-*tyrosine*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CHO,H_2O,$$

which has m. p. 171—174° (decomp. corr.) in the anhydrous state and $[\alpha]_D^{20}$ $+84\cdot9°$ in alcoholic solution. C. S.

Preparation of Alkyl Dialkylmalonamates. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 182045).—The alkyl dialkylmalonamates are employed in the production of the dialkylbarbituric acids. *Ethyl diethylmalonamate*, $NH_2 \cdot CO \cdot CEt_2 \cdot CO_2Et$, needles, m. p. 79°, is preferably produced by alkylating ethyl malonamate in two stages by the repeated action of ethyl iodide in alcoholic sodium ethoxide.

Ethyl dipropylmalonamate, $NH_2 \cdot CO \cdot CPr_2 \cdot CO_2Et$, white needles, m. p. 92°, is prepared by the action of sodium (2 atoms) and propyl iodide (2 mols.) on ethyl malonamate in alcoholic solution.

The alkyl sulphates may also be employed in producing the alkyl dialkylmalonamates. G. T. M.

Production of Alkali Cyanides. Otto Schmidt (D.R.-P. 180118. Compare this vol., i, 299).—By passing nitrogen over a mixture of magnesium, carbon, and an alkali carbonate, an amount of alkali cyanide is obtained equivalent to the quantity of the magnesium present. If, however, the carbonate is replaced by the alkali metal itself, it becomes possible to convert a much larger proportion of alkali metal into cyanide.

$$3Mg + N_2 = Mg_3N_2.$$

$$Mg_3N_2 + 2Na \text{ (Na in excess)} + 2C = 3Mg + 2NaCN.$$

One molecule of magnesium will bring about the transformation of 4 molecules of sodium into sodium cyanide. The magnesium has undoubtedly a specific action on the absorption of nitrogen, and the formation of sodium cyanide occurs far more rapidly and completely than in the absence of this metal. G. T. M.

Glutamine. Ernst Schulze and Ch. Godet (*Landw. Versuchs-Stat.*, 1907, **67**, 313—319. Compare this vol., i, 114).—Fresh preparations of glutamine from (1) sugar-beet and (2 and 3) mangolds gave $[\alpha]_D + 6 \cdot 45°$, $+ 8 \cdot 2°$, and $+ 9 \cdot 5°$ respectively. At 16°, it dissolves in 25·7 parts of water; the copper derivative, $Cu(C_5H_9O_3N_2)_2$, can be obtained in small, bluish-violet crystals by heating a solution of glutamine with copper acetate. The *cadmium* derivative, $Cd(C_5H_4O_3N_2)_2$, obtained by adding freshly precipitated cadmium hydroxide to a heated solution of glutamine until no longer dissolved, separates in fine prisms; when boiled with water, the compound is slowly hydrolysed.

Glutamine (1 mol.) forms a compound with tartaric acid (1 mol.) which separates in rather large, transparent crystals. N. H. J. M.

Calcium Cyanamide. II. Georg Bredig, W. Fraenkel, and E. Wilke (*Zeitsch. Elektrochem.*, 1907, **13**, 605—612. Compare this vol., i, 369).—The influence exerted by various substances on the absorption of nitrogen by calcium carbide has been further studied. Experiments with glucinum, magnesium, and strontium chlorides confirm the view that for metals in the same periodic group the acceleration of the reaction is greater the lower the atomic weight of the metal. This relationship holds for 10% admixture. The formation of cyanide increases, on the other hand, with the atomic weight of the metal, but the quantity is always small. Metallic calcium, magnesium and sodium do not appreciably accelerate the absorption of nitrogen when mixed with the carbide. The view that the nitrogen absorption is directly due to calcium produced from the carbide is not supported by these experiments. Water vapour and calcium oxide, either alone or mixed with other substances, have no influence on the rate of the reaction. The authors suppose that the acceleration phenomena are connected with the fusibility of the added substance and the solubility of the carbide in the flux. For each flux, however, there may be a specific reaction constant. Determination of the velocity of the nitrogen absorption in nitrogen at different pressures shows that this is proportional to the pressure of the gas. Whether diffusion, absorption, or chemical reaction is the determining factor in the velocity of the reaction has not yet been ascertained. H. M. D.

Compounds of Ethylcarbylamine with Cobaltous, Ferrous, and Ferric Chlorides. Karl A. Hofmann and Günther Bugge (*Ber.*, 1907, 40, 3759—3764. Compare this vol., i, 419; Ramberg, *ibid.*, 604).—Guillemard, in another way (this vol., i, 300), has arrived at the authors' conclusion that metallic cyanides are of the carbylamine type.

Cobaltous chloride bisethylcarbylamine, $CoCl_2,2EtNC$, obtained from its constituents in methyl-alcoholic solution, forms green crystals; the chlorine is precipitated completely by silver nitrate. *Ferric chloride bisethylcarbylamine*, $FeCl_3,2EtNC$, similarly obtained in ethereal solution, forms stout, yellow prisms. *Ferric chloride trisphenylcarbylamine*, $FeCl_3,3PhNC$, crystallises in greenish-yellow plates. *Ferric oxychloride tetra-ethylcarbylamine*, $Fe_2OCl_4,4EtNC$, obtained from ferrous chloride and ethylcarbylamine in ether, forms yellow plates. *Ferric oxychloride penta-ethylcarbylamine*,

$$Fe_2OCl_4,5EtNC,$$

is obtained in golden-yellow crystals from a 6% methyl-alcoholic solution of ferrous chloride and ethylcarbylamine (3 mols.).

All these compounds are decomposed by alkalis, but the last-mentioned exhibits its greater stability in giving a precipitate with silver nitrate only in the presence of dilute nitric acid, and in forming Prussian-blue only in the presence of hydrochloric acid. C. S.

Cobalt Dioximines. II. Leo Tschugaeff (*Ber.*, 1907, 40, 3498—3504. Compare Abstr., 1906, i, 814).—Since metal-ammonia derivatives, which contain all the components of the complex molecules in the non-ionisable form, are of especial interest, the author describes two general reactions for preparing compounds of this type.

The compounds $[CoNH_3ClD_2H_2]$ and $[CoD_2H_2NH_3NO_2]$ (where $DH_2 = R^1{\cdot}C(\colon N{\cdot}OH){\cdot}C(\colon N{\cdot}OH){\cdot}R^2$), obtained by the interaction of dimethylglyoxime with derivatives of the pentammine series, $[Co5NH_3Cl]X_2$ and $[Co5NH_3NO_2]X_2$, in the presence of an excess of ammonium acetate have already been described.

It is found that the presence of an excess of acid is important for the success of this reaction in order to prevent the formation of a derivative of the diammine series, thus: $[CoNH_3XD_2H_2] + NH_3 = [Co2NH_3D_2H_2]X$.

Bromopentammine bromide reacts with dimethylglyoxime, thus: $[Co5NH_3Br]Br_2 + 2DH_2 = [CONH_3BrD_2H_2] + 2NH_4Br + 2NH_3$. The resulting *compound* is a typical non-electrolyte and reacts very slowly with silver nitrate in the cold; it separates from dilute acetic acid in glistening, reddish-brown needles; its solution in concentrated sulphuric acid is red.

The *compound* $[CoNH_3(NO_2)D_2H_2]$, obtained by the interaction of the xantho- or *iso*xantho-salts, $[Co5NH_3NO_2]X_2$, and methylethylglyoxime, separates from alcohol in yellowish-brown crystals and is also a non-conductor. The *compound* $[CoNH_3D_2H_2Cl]$ was also obtained from methylglyoxime and purpureo-cobalt chloride, $[Co5NH_3Cl]Cl_2$. The reaction failed when an attempt was made to prepare the compound $[CoD_2H_2NH_3NO_3]$. The compound $[Co2NH_3D_2H_2]NO_3$ was the only product of the action of dimethylglyoxime on the pentammine nitrate, $[Co5NH_3NO_3](NO_3)_2$.

The *compound* $[CoNH_3ID_2H_2]$, obtained from dimethylglyoxime and roseopentammine iodide, $[Co5NH_3H_2O]I_3$, crystallises in dark brown needles. The iodine atom in this compound is not so firmly bound as in the corresponding chloro- and bromo-compounds. When heated with dilute ammonia at 100°, it forms the *compound* $[Co2NH_3D_2H_2]I$, an iodide of the diammine series, which contains an ionisable iodine atom.

The behaviour of the roseo-iodide in comparison with the corresponding chloro- and bromo-salts is remarkable, since the bromide gives with dimethylglyoxime only traces of the compound $[CoNH_3BrD_2H_2]$, whilst the roseo-chloride does not give the compound $[CoClNH_3D_2H_2]$.

The praseo-halogen salts of the tetrammine series, $[Co4NH_3Cl_2]Cl$ and $[Co4NH_3Br_2]Br$, behave towards dimethylglyoxime like the corresponding pentammine compounds, giving the *compounds* $[CoClNH_3D_2H_2]$ and $[CoBrNH_3D_2H_2]$. The isomeric croceo- and flaveo-salts appear to behave similarly, and are at present under investigation.

Another method for preparing the compounds in question is described. A process of autoxidation takes place between 1 mol. of cobalt salt and 1 mol. of dimethylglyoxime in alcoholic solution and in the presence of pyridine, or a similar base in the presence of air. The formation of the *compound* $[CoClPyD_2H_2]$ is expressed by the equation: $2CoCl_2 + 4DH_2 + 4Py + O = 2[CoClPyD_2H_2] + 2PyHCl + H_2O$. The reaction was also conducted with α-picoline, *iso*quinoline, and acridine. In addition to the chlorine atom, there may be substituted bromine or iodine atoms or the electronegative groups, NO_2, SCN, NCO, and N_3. For dimethylglyoxime, other 1:2-dioximes, for example, methylethylglyoxime, may be substituted. The compounds obtained are crystalline and brown to reddish-brown in colour; they are soluble in water with difficulty and exhibit properties typical of non-electrolytes. The *compound* $[CoPyClD_2H_2]$ forms yellowish-brown crystals. The *compounds* $[CoPyNCOD_2H_2]$ and $[CoPyN_3D_2H_2]$ are the first metal ammine derivatives of cyanic acid and hydrazoic acid respectively known which are non-conductors. The compound $[CoPyN_3D_2H_2]$ forms reddish-brown crystals and is very stable. The following derivatives of dimethylglyoxime have been prepared: $[CoNH_3ClD_2H_2]$, $[CoNH_3BrD_2H_2]$, $[CoNH_3ID_2H_2]$, $[CoNH_3NO_2D_2H_2]$, $[CoPyClD_2H_2]$,

$[CoPyID_2H_2]$, $[CoPyNO_2D_2H_2]$, $[CoPySCND_2H_2]$, $[CoPyNCOD_2H_2]$, $[CoPyN_3D_2H_2]$, [Co *iso*quinoline ClD_2H_2], [Co acridine ClD_2H_2].

The following derivatives of methylethylglyoxime have been prepared: $[CoNH_3NO_2D_2H_2]$ and $[CoPySCND_2H_2]$. The following derivative of methylglyoxime has been prepared: $[CoClNH_3D_2H_2]$.

A. McK.

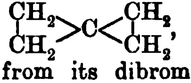
Action of Nitrous Oxygen Compounds with Organo-zinc and -magnesium Compounds. IWAN J. BEWAD (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 947—973. Compare Abstr., 1900, i, 629; this vol., i, 671).

—The group $-N{:}O$ in organic nitrites behaves towards zinc alkyls similarly to the $>C{:}O$ group in aldehydes, consequently nitrosyl chloride and zinc ethyl react thus: $O{:}NCl + Zn(C_2H_5)_2 \longrightarrow ZnEt{\cdot}O{\cdot}NEt_2 \longrightarrow OH{\cdot}NEt_2$ from analogy to $O{:}CCl_2$, which also forms $OH{\cdot}CEt_3$. The β-diethylhydroxylamine thus produced is identical with the product obtained by the action of zinc ethyl on organic nitrites. An abstract of the rest of this paper has already appeared (this vol., i, 671).

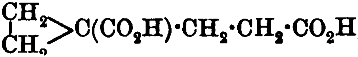
Z. K.

Spirocyclanes. HERMANN FECHT (*Ber.*, 1907, **40**, 3883—3891. Compare Baeyer, Abstr., 1901, i, 135, for nomenclature).

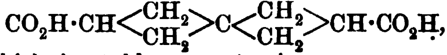
—Vinyltrimethylene (Abstr., 1896, i, 669) is in reality spiro*pentane*,



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\\|\\CH_2\end{matrix},$$

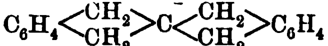
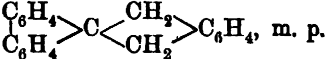
for the nitrile, obtained from its dibromide, yields on hydrolysis *aa-ethyleneglutaric acid*,  $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, m. p. 162°, identical with the acid prepared from ethyl glutaconate, ethylene dibromide, and sodium ethoxide in alcoholic solution.

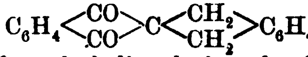
The reaction between pentaerythritol tetrabromohydrin, sodium, and methyl malonate in boiling amyl-alcoholic solution leads ultimately to the formation of spiro*heptanedicarboxylic acid*,

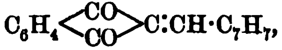


$$CO_2H{\cdot}CH<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>CH{\cdot}CO_2H,$$

m. p. 210°, which is stable to potassium permanganate, bromine, hydrobromic acid at 150°, and fused potassium hydroxide.

Pentaerythritol tetrabromohydrin, benzene, and aluminium chloride react on the water-bath to give, in very bad yield, a deep yellow *hydrocarbon*, m. p. 148°, and a pale yellow, fluorescent *hydrocarbon*, m. p. 161°. The formula  $C_6H_4<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>C_6H_4$ is not ascribed to either of these substances, because their properties are not analogous to those of *xylylenefluorene*,  $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>C_6H_4$, m. p. 220°, which is prepared from fluorene, *o*-xylylene dibromide, and potassium hydroxide at 230°, crystallises in colourless, refractive needles, and is stable to acids or alkalis.

Xylylenediketohydrindene,  $C_6H_4<\!\!\begin{matrix}CO\\CO\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>C_6H_4$, m. p. 150°, is obtained by the addition of an alcoholic solution of sodium ethoxide to *o*-xylylene dibromide and diketohydrindene dissolved in ethyl acetate; it crystallises in yellow needles, decomposes by warming with alkalis, develops a violet colour with concentrated sulphuric acid, and in hot alcoholic solution changes to a yellow *polymeride*, m. p. 245° (decomp.). The *dioxime* has m. p. 215°; the yellow *phenylhydrazone* has m. p. 177°, and the brown *diphenylhydrazone*, $C_{29}H_{24}N_4$, has m. p. 225°. 2-o-*Methylbenzylidenediketohydrindene*,



$$C_6H_4{<}\substack{CO\\CO}{>}C{:}CH{\cdot}C_7H_7,$$

m. p. 156°, forms pale yellow needles, gives a yellow colour with concentrated sulphuric acid, and does not show any tendency to polymerise. C. S.

Preparation of *tert.*-Butyltoluene and *tert.*-Butylxylene. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 184230).—*tert.*-Butyl-*m*-xylene, employed in the production of artificial musk, is obtained in almost theoretical amount by passing *iso*butylene gas through a mixture of *m*-xylene and aluminium chloride to which some *iso*butyl chloride has been added, or into which hydrogen chloride has been introduced. *iso*Butyl bromide or hydrogen bromide may also be employed to start the reaction, and *tert.*-butyltoluene may be produced in a similar manner. The aluminium chloride may be replaced by other condensing agents, such as the chlorides of magnesium, zinc, or iron; the corresponding bromides may also be employed. G. T. M.

Reductions with Amorphous Phosphorus. III. Action of Amorphous Phosphorus and Hydrochloric Acid, D 1·19, on Nitrobenzene. THEODOR WEYL (*Ber.*, 1907, **40**, 3608—3612. Compare this vol., i, 118, 305).—Nitrobenzene is reduced to only a very small extent when heated with red phosphorus and hydrochloric acid, D 1·19, at temperatures not above 140°, but at 140—160° considerable amounts of aniline and *p*-chloroaniline are formed. In one experiment, 75% of the nitrobenzene entering into the reaction formed *p*-chloroaniline.

As aniline and *p*-chloronitrobenzene do not form chloroaniline when heated with phosphorus and hydrochloric acid, D 1·19, at temperatures up to 220°, but according to Bamberger, Büsdorf, and Szolayski (Abstr., 1899, i, 341) *p*-chloroaniline is formed by the action of hydrochloric acid on phenylhydroxylamine or on nitrosobenzene, one or both of these substances must be formed intermediately in the reduction of nitrobenzene by phosphorus and hydrochloric acid.

Whilst aniline gives the well-known violet-purple coloration with calcium hypochlorite in aqueous, but a yellow coloration in acetone, solution, *o*- and *m*-chloroaniline give no coloration in aqueous, but a yellow becoming brown in acetone, solution, and *p*-chloroaniline gives a reddish-brown in both solvents.

p-Chloroacetanilide has m. p. 182° (172·5°; Beilstein and Kurbatoff, this Journ., 1877, i, 473). G. Y.

Mercury Derivatives of *o*-Nitrotoluene. Arnold Reissert (D.R.-P. 182217, 182218).—An aqueous suspension of *o*-nitrotoluene when heated for eight hours with freshly precipitated mercuric oxide and 30% sodium hydroxide solution, or an equivalent amount of some other alkali hydroxide or carbonate, furnishes a *mercury* derivative soluble in aqueous alkali hydroxides and precipitated as a very voluminous, yellow mass on addition of dilute acids, including carbonic acid. The *hydrochloride* of this product is obtained in a crystalline form in colourless needles, m. p. 145—158°, by precipitating an ammoniacal solution with hydrochloric acid. The compound contains mercury and *o*-nitrotoluene in the proportion of one atom of the former to two molecules of the latter.

A sparingly soluble *dimercury* derivative is obtained by prolonging the boiling with mercuric oxide until a product insoluble in hydrochloric acid is obtained. The new compound contains one *o*-nitrotoluene residue combined with two atomic proportions of mercury. The sparingly soluble pale yellow chloride is decomposed by dilute aqueous sodium hydroxide, the free dimercury derivative is dissolved in dilute acetic acid, and reprecipitated by alkali as a heavy, microcrystalline, yellow mass, which explodes on heating, and when gradually warmed decomposes above 220° without melting. It also dissolves in dilute nitric or sulphuric acid, but is insoluble in ammonia.

G. T. M.

Salts and Esters of Benzenesulphonitroanilide. St. Opolski (*Ber.*, 1907, **40**, 3528—3536).—Benzenesulpho-*o*-nitroanilide, m. p. 102—103·5°, forms pale yellow or almost colourless, microscopic crystals, and dissolves in alcohol or benzene with a yellow coloration. The *ammonium* salt is yellow; the *sodium* salt orange, m. p. 230°, to a red liquid: when freshly made and cooled to − 70° it becomes yellow. The same yellow salt is formed on the addition of sodium ethoxide to a cooled ethereal solution of the *o*-nitroanilide; it becomes orange when rubbed with a glass-rod, but is obtained in silky, glistening, yellow needles when slowly crystallised, or in the orange modification when crystallised quickly.

The *thallium* salt is likewise orange when prepared warm, and yellow when made at lower temperatures; it melts to a red liquid at 150°, which becomes orange again when it solidifies.

The *lithium*, *potassium*, *rubidium*, and *mercury* salts were obtained in one, the yellow, form only; the *silver sodium* double salt is also yellow.

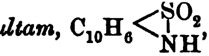
Benzenesulphomethyl-o-*nitroanilide*, $C_6H_5{\cdot}SO_2{\cdot}NMe{\cdot}C_6H_4{\cdot}NO_2$, forms colourless crystals, m. p. 116—117°, and gives colourless solutions.

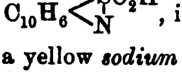
Benzenesulpho-*m*-nitroanilide forms colourless crystals, m. p. 136—137° (Lellmann, Abstr., 1883, 807, describes it as yellow crystals, m. p. 131—132°). The *ammonium* salt is yellow, likewise the *sodium* and potassium salts, which retain this colour on heating and show no tendency to form the red modification. *Benzenesulphomethyl*-m-*nitroanilide* is colourless, m. p. 82—83°. *Benzenesulpho-*

p-nitroanilide, m. p. 139—140°, is colourless and forms yellow salts only; the *methyl* ester, m. p. 120—121°, is also colourless.

Both the *o*- and *p*-benzenesulphonitroanilides are converted by nitric acid into the same *trinitro*-derivative, $C_6H_5{\cdot}SO_2{\cdot}NH{\cdot}C_6H_2(NO_3)_3$, m. p. 210—211°, crystallising in almost colourless needles which give yellow solutions in acetone. E. F. A.

Action of Phosphorus Oxychloride on 1-Naphthylamine-8-sulphonic Acid. FREDERIC DANNERTH (*J. Amer. Chem. Soc.*, 1907, **29**, 1319—1328).—On heating 1-naphthylamine-8-sulphonic acid with concentrated sulphuric acid, Dressel and Kothe (Abstr., 1894, i, 608) obtained the sulphonic acid of an inner anhydride which they termed naphthasultam. They were unable to obtain the naphthasultam itself, since the anhydride formation was always accompanied by sulphonation in the nucleus. This has now been effected, however, by the action of phosphorus oxychloride on potassium 1-naphthylamine-8-sulphonate, a yield of 60% of the theoretical being obtained.

1 : 8-*Naphthasultam*,  $C_{10}H_6<\begin{matrix}SO_2\\ |\\ NH\end{matrix}$, m. p. 177—178°, crystallises from hot water in needles and dissolves in many organic liquids to form solutions with an apple-green fluorescence. The *methyl* derivative, m. p. 125°, and the *ethyl* derivative, m. p. 85°, are crystalline, and yield fluorescent solutions; the former, when heated with potassium hydroxide, is converted into 1-methylnaphthylamine-8-sulphonic acid, thus proving that the methyl group is attached to the nitrogen atom. Naphthasultam forms yellow salts of the alkali earth metals, gives dark blue precipitates with potassium dichromate and ferric chloride, and when treated with nitrous acid is converted into a red, crystalline substance. The *sodium* salt condenses with diazo-compounds to form dyes. *Dibromonaphthasultam*, m. p. 239°, is a white compound which turns blue when boiled with alcohol. *Nitronaphthasultam*, m. p. 253°, forms white crystals which gradually become yellow. The 2 : 4-*dinitro*-derivative, m. p. 259°, forms six-sided prisms; this compound can also be prepared by the nitration of 1 : 8-naphthasultam-2 : 4-disulphonic acid (Dressel and Kothe, *loc. cit.*). 2 : 4-*Diamino*-1 : 8-*naphthasultam* is unstable; its *dihydrochloride* forms slender, pale yellow needles, and its *diacetyl* derivative, m. p. 290°, greenish-yellow needles.

When 1 : 8-naphthasultam is boiled with acetic anhydride, 1 : 8-*iso-naphthasultam*,  $C_{10}H_6<\begin{matrix}SO_2H\\ |\\ N\end{matrix}$, is produced, which forms rhombic crystals and yields a yellow *sodium* salt. When a solution of this compound in methyl alcohol is treated with hydrogen chloride, a *chloro*-derivative, m. p. 200—201°, is produced; the same substance can be obtained by the action of chlorine on *iso*naphthasultam. The *bromo*-derivative, m. p. 162°, is a white, crystalline substance. The *nitro*-derivative, m. p. 212°, forms pale yellow crystals. 2 : 4-*Dinitro*-1 : 8-*iso-naphthasultam*, m. p. 256°, forms yellow crystals; if this compound is heated with sodium hydroxide and the product acidified, the "normal" dinitrosultam is produced.

By the action of fuming nitric acid on either naphthasultam or *iso*-

naphthasultam, 1 : 3-*dinitronaphthalene-5-sulphonic acid* is produced, which does not melt but explodes at about 300°. 1 : 3-Naphthylenediamine-5-sulphonic acid forms black needles, and does not melt when heated. E. G.

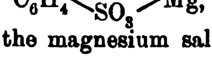
Thiocyanates and *iso*Thiocyanates [Thiocarbimides]. VII. Diphenylcarbamyl Thiocyanate. TREAT B. JOHNSON and L. H. LEVY (*Amer. Chem. J.*, 1907, **38**, 456—461).—When an alkyl halide is treated with ammonium or potassium thiocyanate, an alkyl thiocyanate is first produced, although it sometimes undergoes rearrangement into the corresponding thiocarbimide. In the case of the acyl halides, however, the products of the reaction have always been regarded as thiocarbimides. It has now been found that diphenylcarbamyl chloride reacts smoothly with potassium thiocyanate with formation of diphenylcarbamyl thiocyanate, and it is considered probable that the carbamyl chlorides examined by Dixon (Trans., 1895, **67**, 1040; 1896, **69**, 855, 1593; 1904, **85**, 807) would also yield thiocyanates if treated with potassium thiocyanate under suitable conditions.

Diphenylcarbamyl thiocyanate, $NPh_2 \cdot CO \cdot SCN$, m. p. 138°, forms prismatic crystals, is not affected by hot concentrated hydrochloric acid, and does not react with ammonia or aniline at the ordinary temperature. When heated with thiobenzoic acid, carbon oxysulphide is evolved and *benzoyldithiodiphenylcarbamyl carbamate*,

$$NHBz \cdot CS \cdot S \cdot CO \cdot NPh_2,$$

m. p. 128—129°, is produced, which crystallises in prisms. *Benzoyldiphenylamine*, m. p. 177°, is also formed in this reaction and separates from alcohol in prismatic crystals. The thiocyanate does not show any tendency to undergo rearrangement at the ordinary temperature, but when heated at 150—160°, a thiocarbimide is produced which reacts with ammonia to form diphenylthiobiuret. E. G.

Action of Sulphuric Acid on Phenol. JULIUS OBERMILLER (*Ber.*, 1907, **40**, 3623—3647).—Kekulé (*Ber.*, 1869, **2**, 330) found that the action of concentrated sulphuric acid on phenol at the ordinary temperature leads to the formation of the ortho-, together with traces of the para-, sulphonic acid, whilst at 100—110° the para-acid only is formed. Later authors (Engelhard and Latschinow, *Zeitsch. Chem.*, 1868, **4**, 77; Post, this Journ., 1876, i, 388) have been unable to separate the two sulphonic acids completely by Kekulé's method. The present author has found that the two isomerides may be separated readily by means of the barium or magnesium salts. On evaporation of the aqueous solution of the monobarium salts, $(OH \cdot C_6H_4 \cdot SO_3)_2Ba$, the *o*-sulphonate crystallises out, and the para-acid may be obtained from the mother-liquor by conversion by means of magnesium sulphate into the monomagnesium salt, $(OH \cdot C_6H_4 \cdot SO_3)_2Mg$, which crystallises on further evaporation. The monomagnesium *o*-sulphonate crystallises only with great difficulty, whilst the dimagnesium salt,



$$C_6H_4 < \begin{matrix} O \\ SO_3 \end{matrix} > Mg,$$

is only sparingly soluble; the magnesium salts of the para-acid have the converse solubilities.

Contrary to Kekulé's statements, the *o*-sulphonic acid is not converted into the para-isomeride on prolonged boiling with water, and is only partially transformed on prolonged treatment with concentrated sulphuric acid at the ordinary temperature. The two isomerides form an equilibrium dependent on the temperature and concentration, the formation of the ortho-acid being favoured by low temperatures and dilution of the sulphuric acid. It is probable that even at 100—110° the ortho-acid is not transformed completely. The alkali, alkaline earth, lead, and zinc salts of the pure *o*- and *p*-sulphonic acids, and of phenol-2 : 4-disulphonic acid, are described.

The reaction solution after removal of the *o*- and *p*-sulphonic acids and of the 2 : 4-disulphonic acid, which is formed readily in presence of an excess of sulphuric acid, contains small amounts of an acid, probably phenol-*m*-sulphonic acid (Solomanoff, *Zeitsch. Chem.*, 1869, **5**, 299). This has been isolated in the form of its *monoaluminium*, *monobarium*, and *monomagnesium*, $(OH\cdot C_6H_4\cdot SO_3)_2Mg,8H_2O$, salts, which are described. These three salts give a violet coloration with ferric chloride.

Merck's "aseptol," which is stated to be a 33⅓% aqueous solution of phenol-*o*-sulphonic acid, is found to be a solution of the *p*-sulphonic acid and an amount of the ortho-acid equal to about 6% of the para-acid. G. Y.

Action of *p*-Nitrobenzyl Chloride on *p*-Aminophenol. MARUSSIA BAKUNIN and C. PROFILO (*Gazzetta*, 1907, **37**, ii, 240—250. Compare Abstr., 1906, i, 496).—As already stated (*loc. cit.*), the condensation of *o*- or *p*-aminophenol with benzyl chloride yields mono- or di-substituted derivatives in which the benzyl groups must be regarded as united directly with the amino-nitrogen. By the interaction of *m*-aminophenol (1 mol.) and *o*-nitrobenzyl chloride (2 mols.) in alcoholic solution and in presence of sodium acetate, Lellmann and Mayer (Abstr., 1893, i, 198) obtained a compound to which they ascribed the structure $NO_2\cdot C_6H_4\cdot CH_2\cdot O\cdot C_6H_4\cdot NH\cdot CH_2\cdot C_6H_4\cdot NO_2$; from the authors' results, it must be held that substitution occurs in the amino- and not in the hydroxyl-group of the *m*-aminophenol.

p-*Nitrobenzyl*-p-*aminophenol*, $OH\cdot C_6H_4\cdot NH\cdot CH_2\cdot C_6H_4\cdot NO_2$, obtained by the interaction of *p*-nitrobenzyl chloride and *p*-aminophenol in alcoholic solution, crystallises from water in silky, yellow, hydrated $(+H_2O)$ needles; from alcohol in yellow, micaceous, hydrated $(+H_2O)$ scales, m. p. 86—87°, and from anhydrous benzene or chloroform in brownish-red crystals, m. p. 114—115°. The *hydrochloride*,

$$C_{18}H_{12}O_3N_2,HCl,$$

has m. p. 191°.

Di-p-*nitrobenzyl*-p-*aminophenol*, $OH\cdot C_6H_4\cdot N(CH_2\cdot C_6H_4\cdot NO_2)_2$, also obtained in the reaction between *p*-nitrobenzyl chloride and *p*-aminophenol in alcohol, separates from alcohol in red, acicular crystals, m. p. 179—180°. The *hydrochloride*, $C_{20}H_{17}O_5N_3,HCl$, m. p. 204°, is readily hydrolysed by water.

Phenyl p-*nitrobenzyl*-p-*aminobenzoate*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot CO_2Ph,$$

prepared by the interaction of *p*-nitrobenzyl chloride and *p*-aminophenyl benzoate, separates from benzene in crystals, m. p. 218—220°. The *hydrochloride*, $C_{20}H_{16}O_4N_2$,HCl, m. p. 110—112°, readily undergoes change.

Benzoyl-p-*nitrobenzyl*-p-*aminophenol*, $OH\cdot C_6H_4\cdot NBz\cdot CH_2\cdot C_6H_4\cdot NO_2$, prepared by the action of benzoyl chloride on *p*-nitrobenzyl-*p*-aminophenol in benzene solution, crystallises from alcohol in yellow needles, m. p. 208—210°.

p-Nitrobenzyl-*p*-aminophenol gives a violet coloration with ferric chloride and water and a red coloration with Liebermann's reagent and acetic acid. Di-*p*-nitrobenzyl-*p*-aminophenol, being insoluble in water, gives no colour with ferric chloride and water, but its hydrochloride gives a violet coloration; both the base and its hydrochloride give a red colour with Liebermann's reagent and acetic acid. Neither phenyl *p*-nitrobenzyl-*p*-aminobenzoate nor its hydrochloride gives a coloration with ferric chloride, but both yield red colorations with Liebermann's reagent. Benzoyl-*p*-nitrobenzyl-*p*-aminophenol gives no coloration with ferric chloride, possibly owing to its insolubility, but it yields the characteristic red coloration with Liebermann's reagent.

T. H. P.

Binary Solution Equilibrium between Carbamide and the Three Isomeric Cresols. ROBERT KREMANN (*Monatsh.*, 1907, **28**, 1125—1136. Compare Abstr., 1906, ii, 268).—The melting-point curve for mixtures of carbamide and *p*-cresol falls from the m. p. of carbamide to a break at 25·5°, and then to a eutectic point at 20°, representing mixtures containing 21·5 mol. % and 15 mol. % of carbamide respectively; within these limits of temperature and concentration, carbamide and *p*-cresol form a molecular compound. Mixtures of *p*-cresol-carbamide and carbamide and of *p*-cresol-carbamide and *p*-cresol exist in the solid phase below 25·5° and 20° respectively; above these temperatures, but below the m. p.'s of carbamide and *p*-cresol, the liquid phase is in contact with the one solid component.

Carbamide forms molecular compounds in the same manner, but within wider limits of temperature and concentration, with *o*- and *m*-cresols. The melting-point curve for mixtures of carbamide and *o*-cresol falls from the m. p. of carbamide to a break at about 60°, and then to a eutectic point at about 26°, representing mixtures containing approximately 27·8 mol. % and 10 mol. % of carbamide respectively. The melting-point curve for mixtures of carbamide with *m*-cresol falls to a break at about 65°, and then to a eutectic point at about 2·5°, representing mixtures containing approximately 30 mol. % and 2 mol. % of carbamide.

G. Y.

Derivatives of 6-Nitro-1:3:4-xylenol. RAFFAELE MALTESE (*Gazzetta*, 1907, **37**, ii, 284—288).—6-*Nitro*-4-*methoxy*iso*phthalic acid*, $C_9H_7O_7N$, prepared by oxidising the methyl ether of 6-nitro-1:3:4-xylenol with potassium permanganate, crystallises from water in slender, silky needles, m. p. 230°. The *dimethyl* ester, $C_{11}H_{11}O_7N$, separates from methyl or ethyl alcohol in minute, hard crystals, m. p. 118°. The *monomethyl* ester, $C_{10}H_9O_7N$, crystallises from methyl or ethyl alcohol in minute, white needles, m. p. 190°; the other *mono*-

methyl ester (?) has m. p. 222°. The *monoethyl* ester, $C_{11}H_{11}O_7N$, is deposited from alcohol as a white, crystalline powder, m. p. 108°. The *sodium* salt, $C_9H_5O_7Na_2$, is obtained as a yellow, anhydrous, crystalline powder.

The two *nitromethoxy*-m-*toluic acids* ($NO_2 : OMe = 6 : 4$ and $4 : 6$) have been prepared, but not distinguished. One of them, $C_9H_9O_5N$, separates from water or aqueous alcohol as a yellowish-white powder, m. p. 174°, which is gradually turned red by the action of light; the other isomeride, m. p. 170° (decomp.), is white, and does not redden under the action of light. T. H. P.

Isomerism with Schiff's Bases. Otto Anselmino (*Ber.*, 1907, **40**, 3465—3474).—The author has shown previously (Abstr., 1906, i, 13) that *p*-homosalicylaldehydeanil occurs in two forms, a yellow and a red, which by crystallisation at definite temperatures can be converted one into the other; when dry, the yellow form can be converted by heat into the red, but the reverse change cannot be effected with the dry substance. The effect of pressure is the same as that of heat.

Evidence is submitted to show that these forms are isomeric and not polymorphous. Density determinations gave different values for the two forms; thus, for the yellow form, $D^{17\cdot 1}$ was 1·243, and for the red form 1·262. Solubility determinations in 95% alcohol were carried out at temperatures from 11·8° to 50°. Measurements of the heat of solution in benzene were also made, and the absorption spectra studied. The conclusion is drawn that solutions below 33° contain the yellow form, and above 34° the red.

The behaviour of the anil towards acetyl chloride, acetic anhydride, benzoyl chloride, methyl sulphate, and phenylcarbimide is indicated. When the Grignard action is applied, unchanged anil is obtained at temperatures below 30°; above 40°, the red variety is transformed by the Grignard reagent, but the yellow variety is not. The same relationships with regard to Grignard's reagent hold with salicylaldehydeanil; it is known only in the yellow form, and does not interact, whereas its methyl ether does.

The picrate obtained from the yellow form differs in tint from that obtained from the red form.

The conclusion is drawn that all yellow anils have a similar structure, whereas the red anil in question has the configuration of its ether. Crystallographic measurements also confirmed this view.

The crystalline form of salicylaldehydeanil differs from that of anisaldehyde.

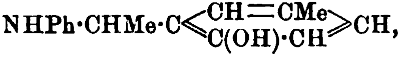
The *acetyl* derivatives of o-*hydroxy*-m-*methylbenzylideneaniline*,

$$C_{18}H_{19}O_4N,$$

separates from light petroleum in needles, m. p. 101°.

o-*Hydroxy*-m-*methylbenzylideneaniline*, $C_{15}H_{15}ON$, prepared by the action of methyl sulphate at 40° on the anil, separates from light petroleum in yellow needles, m. p. 70°.

o-*Hydroxy*-m-*methyl*-a-*anilinoethylbenzene*,



$$NHPh\cdot CHMe\cdot C{<}\begin{matrix}CH{=}CMe\\ C(OH)\cdot CH\end{matrix}{>}CH,$$

obtained by the action of magnesium methyl iodide on the anil, separates from light petroleum in colourless, rectangular leaflets, m. p. 98°.

o-*Methoxy*-m-*methyl-a-anilinoethylbenzene*, $C_{16}H_{19}ON$, obtained from magnesium methyl iodide and the methylated anil, separates from light petroleum in glistening crystals, m. p. 78°.

o-*Hydroxy*-m-*methyl-a-acetylanilinoethylbenzene*, $C_{17}H_{19}O_2N$, separates from light petroleum in nodular crystals, m. p. 123°.

o-*Methoxy*-m-*methyl-a-acetylanilinoethylbenzene*, $C_{18}H_{21}O_2N$, is a syrup.

a-*Anilino*-o-*ethylanisole*, $C_{15}H_{17}ON$, separates from light petroleum in pyramids, m. p. 46°. A. McK.

Preparation of Aminonaphthols. Franz Sachs (D. R.-P. 181333).—The aminonaphthols can be obtained by heating the naphthols or their alkali derivatives with sodamide at 200—210°. The use of the latter compounds reduces the proportion of sodamide required. Naphthalene, quinoline, paraffin, and other heavy hydrocarbons are employed as diluents. Under these conditions, β-naphthol furnishes 5-amino-β-naphthol, whilst α-naphthol yields 5-amino-α-naphthol (compare Abstr., 1906, i, 829 and 949). G. T. M.

Preparation of 8-Arylamino-α-naphtholsulphonic Acids. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 181929).—The 8-amino-α-naphtholsulphonic acids when heated with aromatic amines and their dry hydrochlorides give rise only to tarry products, but when these acids or their alkali salts are heated with aromatic amines in the presence of water, the hitherto unknown 8-arylamino-α-naphtholsulphonic acids are obtained.

Sodium 8-*anilino-α-naphthol*-3 : 6-*disulphonate*,

$$NHPh\cdot C_{10}H_4(OH)(SO_3Na)_2,$$

produced by heating sodium 8-amino-α-naphthol-3 : 6-disulphonate with aniline and water at 120° for forty-eight hours, crystallises from water in spherical aggregates of white needles; the *sodium hydrogen* salt separates in felted, white needles.

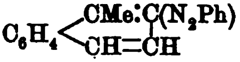
Sodium 8-p-*tolylamino-α-naphthol*-4-*sulphonate*,

$$C_7H_7\cdot NH\cdot C_{10}H_5(OH)\cdot SO_3Na,$$

prepared in a similar manner from sodium 8-amino-α-naphthol-4-sulphonate, *p*-toluidine, and water, crystallises in needles; the free *acid* separates in felted, white needles. The patent contains a tabulated description of ten 8-arylamino-α-naphtholsulphonic acids and other sodium salts. G. T. M.

1 : 2-Methylnaphtha-ψ-quinol. Guido Bargellini and S. Silvestri (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 255—261. Compare this vol., i, 862).—1-Methyl-β-naphthol, when oxidised in acetic acid solution with chromic acid, yields 1 : 2-methylnaphtha-ψ-quinol (compare Fries and Hübner, Abstr., 1906, i, 190).

6-*Bromo*-2-*methoxy*-1-*methylnaphthalene*, $C_{10}H_5BrMe\cdot OMe$, crystallises from acetic acid in white needles, m. p. 65—66° (Fries and Hübner, *loc. cit.*).

2-Benzeneazo-1-methylnaphthalene,  $C_6H_4\left<\begin{matrix}CMe{:}C(N_2Ph)\\ CH{=}CH\end{matrix}\right.$, prepared by the action of phenylhydrazine on 1 : 2-methylnaphtha-ψ-quinol, crystallises from alcohol in orange-red scales, m. p. 79—80° (decomp.), is soluble in ether, ethyl acetate, chloroform, or acetone, and dissolves in concentrated hydrochloric or sulphuric acid to a red solution.

Methylnaphthylazocarbonamide, $C_6H_4\left<\begin{matrix}CMe{:}C{\cdot}N_2{\cdot}CO{\cdot}NH_2\\ CH{=}CH\end{matrix}\right.$, prepared by the action of semicarbazide on 1 : 2-methylnaphtha-ψ-quinol, crystallises from water in orange needles, m. p. 143—144° (decomp.), is readily soluble in ether, acetic acid, or chloroform, and dissolves in concentrated hydrochloric or sulphuric acid giving a green coloration which rapidly turns red.

1 : 2-*Methylnaphtha-ψ-quinoloxime*, $C_{10}H_6Me(OH){:}NOH$, separates from ethyl acetate in crystals, m. p. 140° (decomp.), and dissolves readily in chloroform, benzene, carbon disulphide, or alcohol, and sparingly in light petroleum. By acetic acid, it is decomposed probably in similar manner to the oxime of dimethylnaphtha-ψ-quinol (compare Cannizzaro and Andreocci, Abstr., 1896, i, 488), yielding 2-nitroso-1-methylnaphthalene. Reduction of the oxime by means of zinc dust and acetic acid yields 1-methyl-2-naphthylamine and its acetyl derivative (compare Fries and Hübner, *loc. cit.*). 1-*Methyl-2-naphthylamine hydrochloride* separates in shining scales, m. p. 245° (decomp.). T. H. P.

Condensation Products of Formaldehyde. J. Breslauer and Amé Pictet (*Ber.*, 1907, **40**, 3784—3786).—Methylphthalimide is formed on heating phthalimide with a 40% solution of formaldehyde in a sealed tube at 150—160°; similarly, methylenedisuccinimide (Bechert, Abstr., 1894, i, 488) is obtained from formaldehyde and succinimide.

Methylene phenyl methyl ether, $OPh{\cdot}CH_2{\cdot}OMe$, is produced by the interaction of phenol and formaldehyde in the presence of sulphuric acid, and by the action of monochloromethyl ether on potassium phenoxide. It is a colourless liquid, b. p. 197—200°, D^{12}_{12} 1·0814, and yields with bromine water a *dibromo*-derivative, $C_8H_8O_2Br_2$, which crystallises in colourless, silky needles, m. p. 112—113°.

The action of formaldehyde on α-naphthol in the presence of potassium carbonate results in the formation of a *substance*, $C_{23}H_{16}O_3$, obtained as a dark brown, amorphous, infusible powder. This on distillation yields a *substance*, $C_{22}H_{16}O$, which forms small, pale yellow crystals, m. p. 79—80°, and gives a deep blue coloration with ferric chloride. W. H. G.

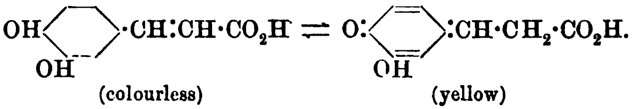
Action of Benzyl Chloride on Resorcinol and Catechol. Marussia Bakunin and P. Alfano (*Gazzetta*, 1907, **37**, ii, 250—252).—The interaction of benzyl chloride and resorcinol in benzene solution in presence of zinc yields: (1) a *compound*, $C_{13}H_{12}O_2$, crystallising from carbon tetrachloride in slender, white needles, m. p. 74—76°; (2) a hydrocarbon crystallising in nacreous laminæ, m. p. 203—206°, and containing 96% of carbon; (3) an oily *compound*, $C_6H_4O_2(CH_2Ph)_2$.

Similarly, benzyl chloride and catechol yield a crystalline compound, m. p. 100°, the nature of which has not yet been determined.

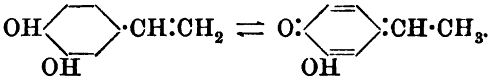
T. H. P.

Cyclic Carbonic Esters of Vinylcatechol. HERMANN PAULY and KARL NEUKAM (*Ber.*, 1907, **40**, 3488—3498).—Pauly has lately shown (this vol., i, 709) that the cyclic esters of catechols are suitable for the isolation of the latter and that protocatechualdehyde carbonate, $CHO\cdot C_6H_3{<}^{O}_{O}{>}CO$, is suitable for the carrying out of syntheses in the catechol group.

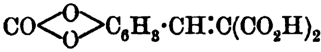
Vinylcatechol carbonate, $CO{<}^{O}_{O}{>}C_6H_3\cdot CH{:}CH_2$, is now described, it being obtained from protocatechualdehyde carbonate by means of the corresponding benzylidenemalonic acid. The latter compound (colourless) is converted by aqueous pyridine into caffeic acid (yellow), thus: $CO{<}^{O}_{O}{>}C_6H_3\cdot CH{:}C(CO_2H)_2 + H_2O = C_6H_3(OH)_2\cdot CH{:}CH\cdot CO_2H + 2CO_2$. The yellow tint of the latter acid is attributed to its partly undergoing the transformation:



Evidence is submitted to show that the free vinylcatechol is an equilibrium mixture of the forms:



3 : 4-*Dioxybenzylidenemalonic acid carbonate*,



$$CO{<}^{O}_{O}{>}C_6H_3\cdot CH{:}C(CO_2H)_2,$$

obtained by heating protocatechualdehyde carbonate, malonic acid, and anhydrous formic acid for nine to ten hours at about 65° in the absence of moisture, separates from glacial acetic acid in colourless needles, m. p. 197° (corr., decomp.), and is sparingly soluble in cold water; its aqueous solution exhibits a violet fluorescence; its solution in concentrated sulphuric acid is lemon-yellow. When boiled with acetic anhydride, it evolves carbon dioxide vigorously and gives a compound, m. p. about 245°. On account of the sensitiveness of the CO_3 group, the acid could not be further characterised by means of its salts.

Vinylcatechol carbonate, prepared by the dry distillation of the preceding acid in an apparatus which is described in detail, separates from a mixture of light petroleum and ether in colourless, glistening prisms, m. p. 65—66°; it has a very intense odour. Although it decolorises a solution of bromine in carbon disulphide almost immediately, a dibromide could not be obtained on account of the ease with which hydrogen bromide is eliminated after the addition. It gives a brownish-yellow coloration with ferric chloride and a violet-brown coloration with sodium carbonate; its solution in concentrated sulphuric acid is reddish-orange. Its solution in alkalis is dark yellow.

A. McK.

Reduction of Safrole and *iso*Safrole. J. TH. HENRARD (*Chem. Weekblad*, 1907, 4, 630—632. Compare Klages, Abstr., 1899, i, 585; Ciamician and Silber, Abstr., 1890, 965, 966, 1294; Eykman, Abstr., 1890, 244; and Jacobsen, Abstr., 1878, 732).—The author has reduced safrole and *iso*safrole with nickel and hydrogen by Sabatier and Senderens's method. The reduction was never quantitative, the product always containing unchanged safrole or *iso*safrole. The reaction product was agitated with dilute sodium hydroxide, and the residual oil, containing unchanged safrole and *iso*safrole along with the dihydro-product, fractionated, the bulk distilling at 228°. The alkaline liquid contained *m*-propylphenol, formed by reduction of the dihydrosafrole with elimination of the para-hydrogen atom. The *m*-propylphenol could not be obtained crystalline, although Jacobsen gives its m. p. as 26°.

A. J. W.

Formation of *s*-Dihydroxydiphenylmethanes. KARL AUWERS [and, in part, FR. JESCHECK and C. KIPKE] (*Annalen*, 1907, **356**, 124—151).—It has been shown previously that hydroxybenzyl bromides and their transformation products readily undergo reactions leading to the formation of substances formulated at first as derivatives of stilbene, but later considered to be derivatives of diphenylmethane (Abstr., 1903, i, 631; 1904, i, 487). The constitution of only one of these derivatives, 3 : 5 : 3′ : 5′-tetrabromo-4 : 4′-dihydroxydiphenylmethane formed from 3 : 5-dibromo-4-hydroxybenzyl bromide, has been definitely established. As some of these derivatives decompose into compounds containing a single benzene nucleus, and that with an ease not to be expected of derivatives of diphenylmethane, it was necessary to establish the constitution also of one of these comparatively unstable products. This has been achieved now in the case of the product obtained from 3-bromo-4-hydroxy-2 : 5-dimethylbenzyl bromide, already shown (*loc. cit.*) not to be identical with 4 : 4′-dihydroxytetramethylstilbene. It is now found identical with 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane,

$$CH_2(C_6H_2Me_2{\cdot}OH)_2,$$

prepared by diazotisation of 4 : 4′-diamino-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane, $CH_2(C_6H_2Me_2{\cdot}NH_2)_2$, which is obtained by transformation of methylenedi-*p*-xylylamine, $CH_2(NH{\cdot}C_6H_3Me_2)_2$.

Methylenedi-p-*xylylamine*, $C_{17}H_{22}N_2$, prepared by shaking *p*-xylidine with formaldehyde in aqueous solution, crystallises in glistening needles, m. p. 67—68°, and when heated with 2 mols. of *p*-xylidine hydrochloride and ½ mol. of *p*-xylidine in a reflux apparatus on the water-bath, is transformed into 4 : 4′-*diamino*-2 : 5 : 2′ : 5′-*tetramethyldiphenylmethane*, $C_{17}H_{22}N_2$, which separates from benzene as a colourless, crystalline powder, m. p. 138—139°. When diazotised with sodium nitrite and boiled in hydrochloric acid solution, this yields 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane, m. p. 181°.

The following substances were prepared in the course of endeavours to synthesise dihydroxytetramethyldiphenylmethane by other reactions.

3 : 5-*Dibromo-4-methoxybenzyl bromide*, $C_8H_7OBr_3$, prepared by the action of hydrogen bromide on 3 : 5-dibromo-4-methoxybenzyl methyl ether in glacial acetic acid solution, crystallises in yellow needles, m. p. 66—67°. 4 : 4′-Dimethoxybenzophenone, m. p. 143—144°, is readily obtained by the action of carbonyl chloride on anisole in carbon tetrachloride solution in presence of aluminium chloride. The action of methylal on *p*-xylene in glacial acetic-sulphuric acid solution leads to the formation of a *substance*, $C_{17}H_{20}$, m. p. 149°; the comparatively high temperature at which this melts makes it probable that it is not dixylylmethane. On treatment with cold fuming nitric acid, it yields a yellow, crystalline *derivative*, m. p. 183°.

The product from 3-bromo-4-hydroxy-2 : 5-dimethylbenzyl bromide having been shown to be 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane, analogous constitutions must be ascribed to the products obtained similarly from other benzyl bromides. Thus the substance, m. p. 234°, described previously as tetrabromodihydroxytetramethylstilbene (Abstr., 1896, i, 150), must be 2 : 5 : 2′ : 5′-tetrabromo-4 : 4′-dihydroxy-3 : 6 : 3′ : 6′-tetramethyldiphenylmethane; the *diacetate*, $C_{21}H_{20}O_4Br_4$, crystallises in needles, m. p. 224—225°. The constitution of this tetrabromo-compound is confirmed by its reduction by means of sodium and boiling amyl alcohol to dihydroxytetramethyldiphenylmethane. The supposed bromide, m. p. 179° (Abstr., 1896, i, 422), is now found to be tribromo-*p*-xylenol.

Similarly, the substance, m. p. 232°, described previously as tetrabromodihydroxytetramethylstilbene (Abstr., 1899, i, 33), must be 2 : 6 : 2′ : 6′-tetrabromo-4 : 4′-dihydroxy-3 : 5 : 3′ : 5′-tetramethyldiphenylmethane.

The conditions under which derivatives of dihydroxydiphenylmethane are formed from hydroxybenzyl bromides and their transformation products, and the mechanism of the reactions concerned, are discussed. The following new details are given.

Whilst the action of water or alkalis on 4-hydroxy-3-aldehydobenzyl bromide leads to the formation of hydroxymethylsalicylaldehyde, 4 : 4′-*dihydroxy*-3 : 3′-*dialdehydodiphenylmethane*,

$$CH_2[C_6H_3(CHO)\cdot OH]_2,$$

m. p. 140°, was obtained on one occasion by long exposure to moist air of the residues from the preparation of the bromide.

2 : 2′-Dihydroxy-3 : 5 : 6 : 3′ : 5′ : 6′-hexamethyldiphenylmethane, m. p. 170° (Zincke and Honorst, this vol., i, 614), is formed when trimethylsaligenin is boiled with slightly acidified water.

The product, m. p. 183—184°, obtained on treating dibromo-*p*-hydroxy-ψ-cumenol with sodium amalgam in alkaline solution (Auwers and Baum, Abstr., 1897, i, 34), is found to be 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane.

Whilst readily decomposed by acids or water, dipiperidylmethane and its compounds remain unchanged when boiled with anhydrous solvents such as toluene. When heated with carbon disulphide at 100°, the piperidine derivative of 3 : 6-dibromo-4-hydroxy-2 : 5-dimethylbenzyl alcohol forms the *additive* compound,

$$OH\cdot C_6Me_2Br_2\cdot CH_2\cdot C_5NH_{10},CS_2,$$

which crystallises in strongly refracting prisms, m. p. 180—181°, but if heated with ether at 100° and then shaken with carbon disulphide the piperidine derivative yields 3 : 6 : 3′ : 6′-tetrabromo-4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane and the *additive* compound of carbon disulphide and dipiperidylmethane, m. p. 58°. G. Y.

Fission of Dihydroxydiphenylmethanes on Bromination. Karl Auwers and Erich Rietz (*Annalen*, 1907, **356**, 152—177).—Whilst hydroxybenzyl bromides readily form the corresponding dihydroxydiphenylmethanes, these tend to decompose into simple benzene derivatives. The two reactions in question differ in that, whereas the first is general, the second has been found to take place markedly only in the case of certain derivatives of dihydroxydiphenylmethane. This paper is a study of the relation of the constitution of dihydroxydiphenylmethanes to their stability on bromination. It is found that, other things being equal, the stability diminishes as the number of methyl groups in the benzene nuclei increases. Thus, on careful bromination (avoidance of an excess of bromine and dilution with a solvent), the carbon chain of 4 : 4′-dihydroxydiphenylmethane and its monomethyl derivative remains unbroken, whilst that of the dimethyl derivative is ruptured to the extent of 2%, and that of the tetramethyl derivative to the extent of 16%. Energetic bromination of the more highly methylated derivatives leads to almost complete rupture of the carbon chain. On the other hand, no decomposition takes place when 3 : 3′-dihydroxydiphenylmethane and its dimethyl derivative are brominated.

It is shown that the rupture of the carbon chain results from the action of the nascent hydrogen bromide; the chain remains intact on bromination in presence of sodium acetate or on treatment of the dihydroxydiphenylmethane with a solution of hydrogen bromide. The following details are new.

4 : 4′-*Dihydroxy*-3-*methyldiphenylmethane*, $C_{14}H_{14}O_2$, prepared by Claus' method (*Diss.*, Marburg, 1901), has m. p. 133°.

The action of boiling aqueous sodium hydroxide on the condensation product of 3 : 5-dibromo-4-hydroxy-2 : 6-dimethylbenzyl bromide with pyridine or diethylamine leads to the formation of a small amount of a yellowish-brown *powder*, $C_{17}H_{16}O_2Br_4$, m. p. 173—175°. Attempts to prepare 4 : 4′-dihydroxy-2 : 6 : 2′ : 6′-tetramethyldiphenylmethane from the corresponding 4 : 4′-*diamino*-compound, $C_{17}H_{22}N_2$, m. p. 205—208°, were unsuccessful.

3 : 3′-*Dihydroxydiphenylmethane*, $C_{18}H_{12}O_2$, prepared from the 3 : 3′-diamino-compound, crystallises in needles, m. p. 103°; the *diacetate*, $C_{17}H_{16}O_4$, crystallises in white leaflets, m. p. 57·5—58·5°.

5 : 5′-*Dihydroxy*-2 : 2′-*dimethyldiphenylmethane*, prepared from the 5 : 5′-diamino-compound, forms white crystals, m. p. 159—160°.

5 : 5′-*Dinitro*-2 : 3 : 2′ : 3′-*tetramethyl*- and 5 : 5′-*dinitro*-2 : 4 : 2′ : 4′-*tetramethyl-diphenylmethanes*, $C_{17}H_{18}O_4N_2$, are obtained as light brown powders, m. p. 164—167° and 173—176° respectively.

The following products are obtained on bromination of the corresponding dihydroxydiphenylmethanes.

3 : 5 : 3′ : 5′-Tetrabromo-4 : 4′-dihydroxydiphenylmethane, m. p. 226—227°, from 4 : 4′-dihydroxydiphenylmethane. 5 : 3′ : 5′-*Tribromo-4 : 4′-dihydroxy-3-methyldiphenylmethane*, m. p. 185—195°, together with traces of a substance, m. p. 42—92°, which may be a mixture of dibromo-*o* cresol and tribromophenol, from 4 : 4′-dihydroxy-3-methyldiphenylmethane. 5 : 5′-Dibromo-4 : 4′-dihydroxydi-*m*-tolylmethane, m. p. 173°, and dibromo-*o*-cresol from 4 : 4′-dihydroxydi-*m*-tolylmethane. 3 : 3′-Dibromo-4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane, m. p. 172°, and dibromo-*p*-xylenol, m. p. 79—80°, from 4 : 4′-dihydroxy-2 : 5 : 2′ : 5′-tetramethyldiphenylmethane. Dibromo-*v*-*m*-xylenol, m. p. 83—85°, from 4 : 4′-dihydroxy-3 : 5 : 3′ : 5′-tetramethyldiphenylmethane. A mixture of tetra- and hexa-bromo-derivatives from 3 : 3′-dihydroxydiphenylmethane. The pure *hexabromo*-derivative, $C_{13}H_6O_2Br_6$, m. p. 241—244°, is formed by the action of an excess of undiluted bromine; the *diacetate*, $C_{17}H_{19}O_4Br_6$, crystallises in needles, m. p. 224°. 4 : 6 : 4′ : 6′-*Tetrabromo*-5 : 5′-*dihydroxy*-2 : 2′-*dimethyldiphenylmethane*, $C_{15}H_{12}O_2Br_4$, m. p. 227—228°, from 5 : 5′-dihydroxydi-*o*-tolylmethane. G. Y.

Preparation of 1 : 3-Dimethylpyrogallol Carbamate. Basler Chemische Fabrik (D.R.-P. 181593).—1 : 3-*Dimethylpyrogallol carbamate*, $C_6H_3(OMe)_2\cdot O\cdot CO\cdot NH_2$, white needles, m. p. 148—152°, has a beneficent action in tuberculosis which is greater than that of 1 : 3-dimethylpyrogallol. This is probably owing to the fact that the latter ether is too rapidly oxidised and eliminated in the form of cœrulignone, whereas the carbamate is only gradually hydrolysed, so that a sustained reaction is rendered possible. The carbamate is prepared by the interaction of 1 : 3-dimethylpyrogallol and carbamic acid chloride in anhydrous ether. G. T. M.

Preparation of Substituted Chlorohydrins. J. D. Riedel, Aktien-Gesellschaft (D.R.-P. 183361).—When epichlorohydrin is subjected to the action of the magnesium derivatives of the aromatic halides, the condensation takes the normal course, and substituted chlorohydrins, $CH_2Cl\cdot CHR\cdot CH_2\cdot OH$, are obtained, where R is an aryl or arylalkyl group.

γ-Chloro-β-phenylpropyl alcohol, $CH_2Cl\cdot CHPh\cdot CH_2\cdot OH$, b. p. 153—154°/28 mm., results from the interaction of epichlorohydrin and magnesium phenyl bromide; it is, however, accompanied by chlorobromopropyl alcohol and phenylchloropropylene.

*γ-Chloro-β-*p*-methoxyphenylpropyl alcohol*,

$$CH_2Cl\cdot CH(C_6H_4\cdot OMe)\cdot CH_2\cdot OH,$$

b. p. 188—189°/25 mm., is the chief product of the interaction of magnesium *p*-methoxyphenyl bromide and epichlorohydrin. *γ-Chloro-β-benzylpropyl alcohol*, $C_6H_5\cdot CH_2\cdot CH(CH_2Cl)\cdot CH_2\cdot OH$, b. p. 165—166°/22 mm., is obtained when magnesium benzyl chloride is employed.

G. T. M.

Cholesterol. III. Transformation of Cholestene. JULIUS MAUTHNER (*Monatsh.*, 1907, **28**, 1113—1124. Compare Abstr., 1906, i, 579—663).—In view of the near relation of the cholesterol group to the terpenes, it appeared probable that, on addition of hydrogen chloride to cholesterol, chloresteryl chloride, and cholestene, a change might take place similar to that of pinene into camphene. This is now found to be the case with cholestene; on loss of hydrogen chloride, cholestene hydrochloride (chlorocholestane) yields a hydrocarbon different from cholestene and termed by the author ψ-cholestene.

Chlorocholestane, formed by the action of hydrogen chloride on cholestene, is obtained in two isomeric modifications, one of which crystallises in rhombic prisms, m. p. 96—97°, $[\alpha]_D^{21}$ + 4·7°, and is the chief product of the reaction. The other crystallises in flat needles, sinters at 70°, and is melted above 80°. Both isomerides yield the same ψ-cholestene.

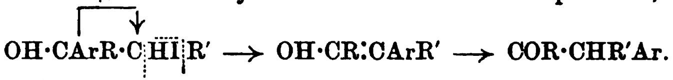
ψ-Cholestene, $C_{27}H_{44}$, formed by boiling chlorocholestane with sodium methoxide and potassium acetate, or by treatment of the chloro-compound with zinc dust and glacial acetic acid or alcoholic silver nitrate, crystallises in flat needles, m. p. 78—79°, $[\alpha]_D$ + 64·86°, and gives the colour reactions of cholestene. The *dibromide*, $C_{27}H_{44}Br_2$, prepared by adding bromine dissolved in glacial acetic acid to the hydrocarbon in ethereal solution, crystallises in colourless, flat needles, m. p. 116—117°, and has $[\alpha]_D^{20}$ + 38·7° immediately after solution in chloroform, $[\alpha]_D^{20}$ + 36·0° after three hours, and $[\alpha]_D^{20}$ + 83·4° after four days, the solution becoming gradually reddish-yellow or dark green with slight red fluorescence, or in benzene immediately after solution $[\alpha]_D$ + 48·0°, after twenty-four hours $[\alpha]_D$ + 47·0°, and after forty-seven days $[\alpha]_D$ + 46·9°, the solution remaining colourless. The mutarotation is probably connected with a *cis-trans* transformation; the initial fall in the rotatory power may result from the dissociation of molecular aggregates. G. Y.

Phytosterol. ADOLF WINDAUS and A. HAUTH (*Ber.*, 1907, **40**, 3681—3686).—A convenient method of separating stigmasterol from phytosterol is described, and a direct comparison of sitosterol and the phytosterol so obtained confirms completely the statement that they are identical (compare this vol., i, 129).

A comparison of the behaviour of cholesterol and phytosterol towards several reagents has been made. *Dihydrophytosterol*, $C_{27}H_{48}O$, prepared by reducing phytosterol with sodium and amyl alcohol, crystallises from acetone in stout needles or rectangular plates, m. p. 175°. This substance does not give the Salkowski colour reaction. Although the substance behaves towards bromine as an unsaturated compound, repeated reduction with sodium and amyl alcohol does not alter the melting point, and therefore the substance must be regarded as a chemical entity. A molecular weight determination of the acetyl derivative shows it to correspond with $C_{29}H_{50}O_2$. *Dihydrophytosteryl chloride*, $C_{27}H_{47}Cl$, forms long, glistening prisms, m. p. 114—115°; on reduction with sodium and amyl alcohol, it yields *dihydrophytostene*, $C_{27}H_{48}$, which crystallises in rectangular leaflets, m. p. 80—81°. Both these compounds behave as unsaturated towards bromine. This state of unsaturation must either be due to the phytosterol not being reduced but only undergoing isomeric change through the intermediary of sodium amyl oxide, or, if reduction has taken place, then phytosterol must contain at least two ethylene linkings. However, on testing phytosterol with sodium amyloxide, there was obtained, not the dihydrophytosterol, but a *ψ-phytosterol*, $C_{27}H_{46}O$, which crystallises in aggregates of needles, m. p. 146—147°. It is indifferent to sodium and amyl alcohol, but it is unsaturated towards bromine, the addition taking place more slowly than with phytosterol. The conclusion is drawn that dihydrophytosterol is a reduction product, and that phytosterol must contain two ethylene linkings, notwithstanding that only 1 mol. of bromine is absorbed.

Whereas cholesterol yields the same saturated substance with sodium amyloxide, or sodium and amyl alcohol, it is probable that it is not a reduction product, but one due to isomeric change; phytosterol, however, gives rise to two different products with these different reagents (compare this vol., i, 610). W. R.

Migration of the Phenyl Group of Aromatic Iodohydrins by Elimination of Hydrogen and Iodine from the Same Carbon Atom. MARC. TIFFENEAU (*Compt. rend.*, 1907, **145**, 593—596. Compare this vol., i., 39).—The author has previously proposed to explain the transformation of aromatic iodohydrins of the type $OH\cdot CArR\cdot CHIR'$ into aldehydes or ketones, when deprived of hydrogen iodide, by (1) loss of hydrogen and iodine from the same carbon atom and migration of the aromatic group, followed by (2) isomeric change of the vinyl alcohol derivative at first produced, thus:



$$OH\cdot CArR\cdot C\,\vdots\,HI\,\vdots\,R' \longrightarrow OH\cdot CR{:}CArR' \longrightarrow COR\cdot CHR'Ar.$$

Study of the ethers of these iodohydrins affords experimental proof of the correctness of this view. Whilst the ethers of the aromatic iodohydrins react with silver nitrate, giving the aldehyde or ketone directly (owing to hydrolysis of the vinyl derivative by the liberated nitric acid), by using mercuric oxide the reaction can be stopped at the end of the first stage. When an ethereal solution of anethole ethyliodohydrin, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot CHMeI$, is shaken with mercuric oxide, the *vinyl ether*, $OMe\cdot C_6H_4\cdot CMe{:}CH\cdot OEt$, is formed. This has b. p. 269—271°, D^0 1·044, and combines directly with bromine. Its lower homologue, $OMe\cdot C_6H_4\cdot CMe{:}CH\cdot OMe$, has b. p. 262—263°, and D^0 1·065. Both are easily converted by acids into *p*-methoxyhydratropaldehyde.

The author considers that the iodohydrins of the type

$$OH\cdot CHAr\cdot CRR'I$$

belong rather to the glycols than to the iodohydrins of the general type, since elimination of hydrogen iodide from the latter leaves a less resistant hydroxyl group, whilst elimination of HI or water from the two former types leaves a more resistant hydroxyl. E. H.

A Product obtained in the Technical Preparation of Benzoic Acid from Coal Tar. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1907, **28**, 1091—1097).—A method of preparing benzoic acid from coal tar has been based (D.R.-P. 109122) on the observation by Krämer and Spilker (Abstr., 1890, 496) of benzonitrile in coal tar freed from phenol and bases. The present paper is an account of the examination of a product obtained together with the benzoic acid. It is found to consist of benzoic esters, chiefly 1 : 3 : 4-xylenyl benzoate, together with small amounts of free phenols and benzoic acid, and traces of coumarone. The crude material for the preparation of the benzoic acid, in spite of having been treated with alkalis, must contain 1 : 3 : 4-xylenol together with not more than traces of phenol and cresol, which on hydrolysis of the benzonitrile esterify part of the benzoic acid. G. Y.

Hyposulphites. IV. ARTHUR BINZ and THEODOR MARX (*Ber.*, 1907, 40, 3855—3860. Compare Abstr., 1904, i, 964; 1905, ii, 521; 1906, ii, 23).—Where benzoyl chloride acts on potassium oxalate, sodium nitrite, or sodium carbonate, it forms benzoic anhydride (Gerhardt; Minunni and Caberti; Deninger), for example:

$$2C_6H_5\cdot COCl + Na_2CO_3 = 2NaCl + CO_2 + (C_6H_5\cdot CO)_2O,$$

the reactions in question taking place with great ease in the presence of pyridine. The action of benzoyl chloride on sodium hyposulphite is similar, benzoic anhydride resulting either in the presence or absence of pyridine. Three additional products are, however, obtained; from benzoyl chloride alone, benzoyl disulphide is produced; from benzoyl chloride and pyridine, in addition to benzoyl disulphide, a red base of the probable formula $C_{11}H_{10}N_2S$, and a yellow compound of a high molecular weight are formed.

The behaviour of benzoyl chloride towards sodium sulphite, both in the absence and presence of pyridine, has also been studied. Benzoyl disulphide is not formed in this case. The change $2C_6H_5\cdot COCl + Na_2SO_3 = 2NaCl + (C_6H_5\cdot CO)_2O + SO_2$ is accompanied by the formation of the red and yellow compounds already mentioned. The latter compounds are also formed by the action of sulphur dioxide on a mixture of benzoyl chloride and pyridine.

The yellow *compound*, to which the formula $C_{23}H_{16}O_6N_4S_4$ is provisionally assigned, is either not dissolved by the ordinary solvents or is transformed into the red *base*, $C_{11}H_{10}N_2S$, which forms ruby-red needles, m. p. 259°. The molecular weight of the latter compound was determined by the cryoscopic method. A. McK.

Preparation of the Alkylamino-esters of *p*-Aminobenzoic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 179627, 180291, 180292).—The esters of aromatic acids are known to possess anæsthetic properties, but only in a few cases is this action of any practical importance, owing to the circumstance that it is somewhat transient and is accompanied by irritant after-effects. It has now been found that the soluble hydrochlorides of the alkylamino-esters of *p*-aminobenzoic acid produce a well-sustained anæsthesia without any disagreeable irritation.

Chloroethyl p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2Cl$, white needles, m. p. 56°, is produced by heating equal quantities of chlorohydrin and *p*-nitrobenzoyl chloride at 120—125°; when heated with piperidine it furnishes *piperidinoethyl* p-*nitrobenzoate*, m. p. 61—62°. *Piperidinoethyl* p-*aminobenzoate*, m. p. 90°, results from the reduction of the preceding ester; its *hydrochloride*, m. p. 213°, crystallises in white needles.

Diethylaminoethyl p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, a viscid oil, is produced by the interaction of chloroethyl *p*-nitrobenzoate and diethylamine. *Diethylaminoethyl* p-*aminonitrobenzoate*, $NH_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, m. p. 51°, crystallises from dilute alcohol with $2H_2O$; hydrochloride, needles, m. p. 156°.

Diethylaminotrimethylcarbinol, $OH\cdot CMe_2\cdot CH_2\cdot NEt_2$, b. p. 55°/11 mm., obtained by the action of magnesium methyl iodide on diethylaminoacetone, yields *diethylaminotrimethylcarbinyl* p-*nitrobenzoate*,

$$NO_2\cdot C_6H_4\cdot CO_2\cdot CMe_2\cdot CH_2\cdot NEt_2,$$

m. p. 47—48°, on treatment with *p*-nitrobenzoyl chloride. *Diethylaminotrimethylcarbinyl* p-*aminobenzoate*, $NH_2\cdot C_6H_4\cdot CO_2\cdot CMe_2\cdot CH_2\cdot NEt_2$, a viscid oil, gives a crystalline hydrochloride, m. p. 183—184°. The patent contains a list of eighteen of these alkylamino-esters of *p*-nitrobenzoic acid with the corresponding esters of *p*-aminobenzoic acid and their hydrochlorides.

Piperidylethyl p-*aminobenzoate*, $NH_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot C_5NH_{10}$, was obtained by dissolving hydroxyethylpiperidine and *p*-aminobenzoic acid in cold concentrated sulphuric acid. The solution was subsequently heated to 90—100°, poured into ice-water, and rendered ammoniacal; the base, m. p. 90°, which is obtained from its crystalline hydrochloride, m. p. 213°, crystallises from light petroleum in needles.

Piperidylethyl p-*dimethylaminobenzoate*,

$$NMe_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot C_5NH_{10},$$

m. p. 45°, was obtained from hydroxyethylpiperidine and *p*-dimethylaminobenzoyl chloride in benzene solution; its hydrochloride, m. p. 205°, is readily soluble in water to a neutral solution. The ester may also be prepared by heating hydroxyethylpiperidine with *p*-dimethylaminobenzoic acid and concentrated hydrochloric acid or by warming this base with *p*-dimethylaminobenzoic anhydride.

The following esters and their hydrochlorides were also prepared: *diethylaminoethyl* p-*diethylaminobenzoate*,

$$NEt_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2,$$

oily; hydrochloride, white needles, m. p. 162—163°: *diethylaminoethyl* p-*aminobenzoate*, $NH_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot NEt_2$, m. p. 51°; hydrochloride, m. p. 156°: *diethylaminoethyl* p-*methylaminobenzoate*, oily; hydrochloride, m. p. 106—109°: *piperidylethyl* p-*methylaminobenzoate*, oily; hydrochloride, m. p. 145—147°: *diethylaminoethyl* p-*ethylaminobenzoate*, oily; hydrochloride, m. p. 119—121°.

These esters, which have important anæsthetic properties, can also be prepared by alkylating *p*-azobenzoic acid or its chloride with the amino-alcohols and then reducing the products.

Piperidylethyl p-*azobenzoate*, m. p. 118—119°, separates in brick-red needles; *diethylaminoethyl* p-*azobenzoate*, m. p. 82°, forms yellowish-red leaflets.

G. T. M.

Preparation of Alkylaminohexyl Benzoates. Chemische Fabrik auf Aktien, vorm. E. Schering (D.R.-P. 181287).—The alkylaminohexyl alcohols on benzoylation furnish a series of complex esters having the general formula $NRR'\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OBz$, where R is an alkyl group and R′ either a hydrogen atom or another alkyl group. These compounds are less toxic than the anæsthetics of the stovaine series, and as their hydrochlorides react as neutral substances, even in concentrated solutions, they are devoid of any irritating action.

γ-Methylamino-αγ-dimethylbutyl benzoate,

$$NHMe\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OBz,$$

is an oily substance produced by treating γ-methylamino-*αγ*-dimethylbutyl alcohol with benzoic anhydride in the presence of water on the water-bath; hydrochloride, needles, m. p. 161—162°.

γ-Ethylamino-αγ-dimethylbutyl benzoate,

$$NHEt\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OBz,$$

oil, prepared from γ-methylamino-*αγ*-dimethylbutyl alcohol hydrochloride and benzoyl chloride, yields a hydrochloride forming small needles, m. p. 172—173°.

γ-Dimethylamino-αγ-dimethylbutyl benzoate,

$$NMe_2\cdot CMe_2\cdot CH_2\cdot CHMe\cdot OBz,$$

and *γ-diethylamino-αγ-dimethylbutyl benzoate* are oils; their hydrochlorides melt at 153—154° and 164—167° respectively.

G. T. M.

Methyl *m*-Amino-*p*-dimethylaminobenzoate. FRÉDÉRIC REVERDIN (*Ber.*, 1907, **40**, 3686—3691; *Arch. sci. phys. nat.*, 1907, **24**, 248—256; *Bull. Soc. Chim.*, [iv], 1, 995—1001).—It has been discovered that during the reduction of methyl nitrodimethylaminobenzoate, the ester is very easily hydrolysed, and accordingly the following compounds must be deleted from the literature. Methylaminodimethylaminobenzoate hydrochloride, m. p. 228°, the acetate, m. p. 232°, the condensation product with chlorodinitrobenzene, m. p. 253—254°, and the methyl hydroxy-*p*-dimethylaminobenzoate of m. p. 176°, and its barium salt (Abstr., 1906, i, 273).

The re-investigation has resulted in the preparation of 3-*acetylamino-4-dimethylaminobenzoic acid*, $C_{11}H_{14}O_3N_2$, which forms glistening leaflets, m. p. 246—247°; the *diacetyl* compound, lamillæ, m. p. 194°; the *picrate*, m. p. 199—200°. 3-*Chloro-4-dimethylaminobenzoic acid*,

$$C_9H_{10}O_2NCl,$$

forms long prisms, m. p. 178—179°; the corresponding *iodo*-compound has m. p. 190—191°, and crystallises in white needles. The *methyl* ester was obtained from the acid, and by reduction of the nitro-derivative with sodium hyposulphite in the cold; it forms prisms, m. p. 56°; the *monacetyl* compound, $C_{12}H_{16}O_3N_2$, has m. p. 103—104°, and the *picrate*, m. p. 187°.

W. R.

Naphtholmonosulphonates of Ethyl *p*-Aminobenzoate. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 181324).—The naphtholmonosulphonates of ethyl *p*-aminobenzoate possess the powerful anæsthetic properties of the amino-ester, and are distinguished from the salts of this substance with the mineral acids by their greater stability and solubility, and also by their neutral character. They are prepared either by the direct interaction of their components or by double decomposition between a metallic naphthol-monosulphonate and ethyl *p*-aminobenzoate hydrochloride.

Ethyl p-*aminobenzoate β-naphthol-6-sulphonate*,

$$OH\cdot C_{10}H_6\cdot SO_3H,NH_2\cdot C_6H_4\cdot CO_2Et,$$

is moderately soluble in hot water, less so in the cold solvent.

G. T. M.

p-Aminocinnamylideneacetic Acid. HERMANN FECHT (*Ber.*, 1907, 40, 3891—3893. Compare following abstract).—p-*Aminocinnamylideneacetic acid* is obtained by the reduction of the nitro-compound by a ferrous salt in ammoniacal solution. In addition to the acid, there is produced an amorphous, dark red substance, insoluble in water, which may be an abnormal ammonium salt. From *o*-aminocinnamylidenemalonic acid, the reddish-yellow hydrogen ammonium salt ($2H_2O$) can be prepared, the aqueous solution of which is decolorised by a few drops of acetic acid or of ammonium hydroxide.

p-Aminocinnamylideneacetic acid, and also methyl *p*-dimethylaminocinnamylideneacetate, form dark red solutions in acetic acid or alcoholic hydrogen chloride, whereas in hydrochloric acid a yellow solution is obtained, from which red crystals of a hydrochloride are isolated; the aqueous solution is decolorised by the addition of hydroxylamine hydrochloride, with the separation of the colourless hydrochloride of an isomeric acid containing $2H_2O$. When the solution of this hydrochloride is boiled in the absence of excess of hydrochloric acid, the yellow, isomeric amino-acid is obtained, which is called the β-acid, in contradistinction to the original *p*-aminocinnamylideneacetic acid, which is called the α-acid. The β-acid forms yellow solutions in alkalis or acetic acid, and colourless solutions in mineral acids. A hydrochloric acid solution in the cold deposits anhydrous colourless crystals of a hydrochloride, but by boiling the solution the red hydrochloride of the α-acid is obtained.

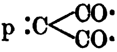
The conversion of the α- into the β-acid is promoted by phenylhydrazine, aminoguanidine, or semicarbazide, as well as by hydroxylamine.

Both the α- and β-acid give the same colourless *acetyl* derivative, m. p. 265° (decomp.).

C. S.

Quinone Formation. Constitution of Triphenylmethane Dyes. HERMANN FECHT (*Ber.*, 1907, 40, 3893—3903. Compare preceding abstract).—To the coloured salts of the *p*-aminocinnamylidene derivatives of acetic and malonic acids, the author ascribes quinonoid formulæ, $NH_2Cl{:}C_6H_4{:}CH\cdot CH{:}CH\cdot CH_2\cdot CO_2H$ and

$$NH_2Cl{:}C_6H_4{:}CH\cdot CH{:}CH\cdot CH(CO_2H)_2.$$

The carboxyl group in these acids has very little auxochromic influence. The pronounced difference in colour which exists between the salts of the two acids in alkaline solution disappears on acidification, because the group  ${:}C\begin{smallmatrix}<CO\cdot\\ \;\;CO\cdot\end{smallmatrix}$, which endows the dicarboxylic acid with its deeper colour, no longer exists in the quinonoid salts which are formed in acid solution.

α-p-*Aminocinnamylideneacetic acid*,

$$NH_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CH{:}CH \cdot CO_2H,$$

m. p. 200° (decomp.), separates from water or alcohol in brownish-yellow needles. The *β-acid*, m. p. 200° (decomp.), forms yellow crystals. They are regarded as stereoisomerides. The red *hydrochloride* of the α-acid has m. p. 260° (decomp.), and the colourless hydrochloride of the β-acid decomposes at 250—260°. The *methyl* esters of the α- and β-acids, obtained by the action of diazomethane, both have m. p. 145—146°. The α-ester in benzene solution yields with alcoholic hydrogen chloride bluish-red needles of the *hydrochloride*, while the β-ester, which is turned red by cold hydrochloric acid, only yields a colourless *hydrochloride* in the presence of hydroxylamine. The tertiary *base*, $C_{14}H_{17}O_2N$, m. p. 142°, obtained from the α-ester and methyl iodide, has the same colour as the non-methylated amino-acid.

o-*Aminocinnamylidenemalonic acid*,

$$NH_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CH{:}C(CO_2H)_2,$$

m. p. 175°, forms orange-yellow needles, and does not yield coloured salts in acid solution; the para-*isomeride*, m. p. 190°, crystallises in brown needles.

as-*Dimethylaminodiphenylethylene*, $CH_2{:}CPh \cdot C_6H_4 \cdot NMe_2$, m. p. 56°, is obtained from *p*-dimethylaminobenzophenone and magnesium methyl iodide, the intermediately-formed *carbinol*, $NMe_2 \cdot C_6H_4 \cdot CPhMe \cdot OH$, has b. p. 202°/14 mm., and loses water at 130°, yielding the preceding compound. Michler's ketone and magnesium methyl iodide yield the *carbinol*, $OH \cdot CMe(C_6H_4 \cdot NMe_2)_2$, m. p. 152°, which crystallises in colourless needles and loses water on heating, forming as-*tetramethyldiaminodiphenylethylene*, $CH_2{:}C(C_6H_4 \cdot NMe_2)_2$, m. p. 124°, b. p. 250°/12 mm., which, like the carbinol, gives a blue solution in acetic acid and yellow solutions in mineral acids.

Benzylidene-p-*dimethylaminoacetophenone*, $NMe_2 \cdot C_6H_4 \cdot CO \cdot CH{:}CHPh$, m. p. 165°, prepared from cinnamanilide, dimethylaniline, and phosphorus oxychloride, crystallises in yellow needles, dissolves in acetic or mineral acids with a yellow colour, and forms a red solution with alcoholic hydrogen chloride. C. S.

Sodium Salicylate. WILHELM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1907, 651—652).—When water is added, drop by drop, to a weighed quantity of sodium salicylate until this just dissolves, it is found that 1 part of the salt dissolves in 1·55 parts of water or 6·45 parts in 10 c.c. In two out of eight experiments made in the reverse way, 6·57 and 6·60 parts of the salt dissolved in 10 c.c. of water, whence it is concluded that this salt shows some tendency to form supersaturated solutions. The specific gravities of a series of solutions of sodium salicylate are given in the original. T. A. H.

Behaviour of Very Weak Acids and Pseudo-acids towards Ammonia. ARTHUR HANTZSCH [and, in part, MISS EDITH MORGAN and HERBERT GORKE] (*Ber.*, 1907, **40**, 3798—3805).—Although simple phenols and naphthols, such as thymol, ψ-cuminol, mesitol, α-naphthol, and β-naphthol, are almost completely converted into ammonium salts when exposed in an atmosphere of ammonia, those phenols and naphthols which contain the "negative" group $-CO_2R$, ortho to the hydroxyl group, such as ethyl salicylate, ethyl α-naphthol-2-carboxylate, and ethyl β-naphthol-1-carboxylate, are practically indifferent towards ammonia at the ordinary temperature. The same retarding effect is produced by an acetyl or benzoyl group in the position ortho to the hydroxyl group. These phenols consequently belong to the group of "cryptophenols" (Auwers, Abstr., 1906, i, 838). Salol (phenyl salicylate) differs somewhat from ethyl salicylate, since it slowly absorbs ammonia to form an ammonium salt. The ammonium salt of ethyl salicylate is formed, however, when ammonia is passed into a solution of the ester in light petroleum or toluene at − 40°. Salicylaldehyde, ethyl *m*-hydroxybenzoate, and ethyl *p*-hydroxybenzoate absorb ammonia to form salts. Salicylic acid absorbs only 1 mol. of ammonia.

A new method for ascertaining whether a compound combines with ammonia in an indifferent solvent to form a salt is described. A known weight of the substance to be examined is dissolved in benzene and the depression of the freezing point observed; the calculated quantity of ammonia in the form of a *N*/10 solution in benzene is then added and the depression again noted. If an ammonium salt is formed, the mol. wt. obtained from the total depression of the freezing point of the benzene will correspond with the mol. wt. of the salt. If no combination has taken place, the value obtained will be the mean of the mol. wts. of ammonia and the substance. When the observed value lies between this mean value and the mol. wt. of the ammonium salt, it denotes the partial formation of an ammonium salt.

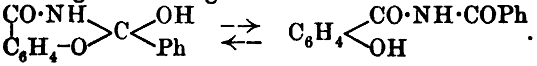
It is stated, in conclusion, that the apparent slow precipitation of the ammonium salts of various compounds recorded by Hantzsch and Dollfus (Abstr., 1902, i, 223) on passing ammonia into solutions of these compounds in benzene is due in some cases to supersaturation, whilst, in others, the crystals of the ammonium salt which separate out at first are so small that they can only be detected by illuminating the solution with a beam of light. The slow precipitation of an ammonium salt in benzene does not therefore indicate the presence of a pseudo-acid. W. H. G.

Acyl Derivatives of Salicylamide and Allied Compounds. KARL AUWERS (*Ber.*, 1907, **40**, 3506—3514).—The author has pointed out previously (Abstr., 1905, i, 894) that the isomeric benzoates of salicylamide described by Titherley and Hicks (Trans., 1905, **87**, 1207) are not desmotropic in the sense of the formulæ:

$$OBz{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$$

(m. p. 144°, labile) and $OBz{\cdot}C_6H_4{\cdot}C(OH){:}NH$ (m. p. 208°, stable), and that the compound with the higher melting point is the *N*-benzoate, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NHBz$.

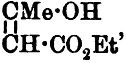
The present paper is a discussion of the more recent work of McConnan and Titherley (Trans., 1906, **89**, 1318); the latter authors are not in agreement with the author's conclusions, and suggest that the higher melting modification exhibits tautomerism in the sense:

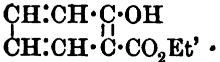


p-*Hydroxybenzamide* O-*benzoate*, $C_{14}H_{11}O_3N$, separates from glacial acetic acid in colourless needles, m. p. 218—220°.

Determinations of the molecular weights of acetyl benzamide, *N*-acetylsalicylamide, and *O*-benzoylsalicylamide respectively in *p*-dibromobenzene solutions are submitted in support of the views advocated.

o-*Benzoyloxyphenylacetamide*, $OBz\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH_2$, obtained by benzoylating *o*-hydroxyphenylacetamide, separates from alcohol in glistening leaflets, m. p. 162—164°. It is insoluble in alkali and is converted by cold concentrated sulphuric acid into the original substance; it is accordingly an *O*-ester. The constitution was proved still further by conversion of the compound into o-*benzoyloxybenzyl cyanide*, $C_{15}H_{11}O_2N$, by means of phosphoric oxide; the latter compound separates from light petroleum in needles, m. p. 50°, and, when hydrolysed, forms o-*hydroxybenzyl cyanide*, which separates from a mixture of light petroleum and benzene in colourless needles, m. p. 117—119°. A. McK.

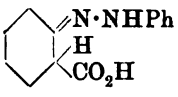
Phenylhydrazone of Salicylic Acid. HUGO SCHRÖTTER AND JOSEF FLOOH (*Monatsh.*, 1907, **28**, 1099—1106. Compare Madsen, this vol., i, 423).—The resemblance of the enolic formula of ethyl acetoacetate,  $\begin{matrix}CMe\cdot OH\\ \|\\ CH\cdot CO_2Et\end{matrix}$, to the formula of ethyl salicylate,



$$\begin{matrix}CH{:}CH\cdot C\cdot OH\\ |\qquad\quad \|\\ CH{:}CH\cdot C\cdot CO_2Et\end{matrix}$$

suggested that the latter or its ketonic form should undergo condensations similar to those of ethyl acetoacetate. This view has led the authors to investigate the action of phenylhydrazine on methyl salicylate.

When heated with 2 mols. of freshly distilled phenylhydrazine and a few drops of piperidine in a reflux apparatus on a water-bath, methyl salicylate forms *salicylic acid-phenylhydrazone*, $C_{13}H_{12}O_2N_2$, in a 10% yield. This crystallises in white leaflets, m. p. 130°, gives a violet coloration when heated with aqueous, or in the cold with aqueous-alcoholic, ferric chloride, reduces ammoniacal silver, platinum chloride, and Fehling's solutions, dissolves in aqueous alkali carbonates, and can be recrystallised from concentrated sulphuric acid. It must have the annexed constitution. The *ammonium* salt exists only in solution; the *potassium*, *sodium*, *calcium*, and *barium* salts readily decompose on recrystallisation or on evaporation of their aqueous solutions. The *piperidine* salt, $C_{18}H_{12}O_2N_2,C_5H_{11}N$, is obtained in a 55—60% yield by heating methyl salicylate and phenylhydrazine with an excess of piperidine; it crystallises in nacreous leaflets, m. p. 162°, is neutral in cold, but alkaline in hot, aqueous solution, and is decomposed slowly at 100° or by prolonged action of steam, or more quickly by aqueous alkalis. G. Y.



Synthesis of Iodogorgonic Acid. HENRY L. WHEELER (*Amer. Chem. J.*, 1907, **38**, 356—358).—Henze (this vol., i, 370) has referred to the iodogorgonic acid prepared by Wheeler and Jamieson (Abstr., 1905, i, 350) as *l*-di-iodotyrosine. It has now been found that the supposed *l*-tyrosine, which, on treatment with iodine, yielded iodogorgonic acid, was really the inactive variety, and that the iodogorgonic acid (di-iodotyrosine) produced was also inactive and identical in every respect with the natural acid. E. G.

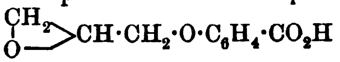
***m*-Hydroxytritanolactone.** HANS VON LIEBIG and PAUL KEIM (*J. pr. Chem.*, 1907, [ii], 76, 275—277. Compare Abstr., 1905, i, 781; this vol., i, 45).—The condensation of benzil with phenol in presence of zinc chloride leads to the formation of a *substance*, crystallising in colourless needles, m. p. 239°, and m-*hydroxytritanolactone*, $C_{20}H_{14}O_2$, which crystallises in rhombic leaflets, m. p. 120°. The *sodium*, $C_{20}H_{15}O_3Na$, *disodium*, $C_{20}H_{14}O_3Na_2$, *potassium*, and *dipotassium* salts have been analysed. Whilst *m*-hydroxytritanolactone remains unchanged on evaporation of its solutions, the alkali salts decompose forming diphenylmethane. *Bromo*-m-*hydroxytritanolactone*, $C_{20}H_{13}O_2Br$, forms colourless, rhombic leaflets, m. p. 129°.

m-*Methoxytritanic acid*, $C_{21}H_{18}O_3$, prepared by hydrolysis of the methyl ester, crystallises in rhombic leaflets, m. p. 235°, and loses carbon dioxide at about 280°. The *potassium* salt, $C_{21}H_{17}O_3K,2H_2O$, crystallises in needles. The *methyl* ester, $C_{22}H_{20}O_3$, forms stout prisms, m. p. 134°.

m-*Ethoxytritanic acid*, $C_{22}H_{20}O_3$, crystallises in needles, m. p. 264°, boils slightly above its m. p. in a vacuum, and loses carbon dioxide when heated under atmospheric pressure. The potassium salt, $C_{22}H_{19}O_3K$, was analysed. The *ethyl* ester, $C_{24}H_{24}O_3$, forms rhombohedra, m. p. 84°.

m-*Methoxytritanol*, $C_{20}H_{18}O_2$, prepared by the action of concentrated sulphuric acid or of lead dioxide and glacial acetic acid on *m*-methoxytritanic acid, remains unchanged when heated at 360° or when boiled with ethereal or alcoholic hydrogen chloride. m-*Methoxytritane*, $C_{20}H_{18}O$, formed by heating *m*-methoxytritanic acid, separates from alcohol in small, rhombic crystals, m. p. 116°. m-*Ethoxytritane* crystallises in large prisms, m. p. 68°. m-*Hydroxytritane*, $C_{19}H_{16}O$, formed by heating the methyl ether or methoxytritanol or ethoxytritane with hydrogen iodide and glacial acetic acid, crystallises in hexagonal leaflets, m. p. 124°. These tritanic acids and tritanol derivatives give a violet coloration with concentrated sulphuric acid; the tritane derivatives give a yellow coloration. Only *m*-hydroxytritanolactone does not give a coloration. G. Y.

The Condensation of Salicylic Acid with Epichlorohydrin or the Dichlorohydrins. MARTIN LANGE (D.R.-P. 184382).—Salicylic acid, when condensed in sodium hydroxide solution with epichlorohydrin or α- or β-dichlorohydrin, gives rise to the soluble sodium salt of a condensation product which corresponds with either of the following formulæ:

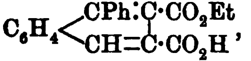


$\begin{matrix}CH_2\\|\\O\end{matrix}\!>CH\cdot CH_2\cdot O\cdot C_6H_4\cdot CO_2H$ or

$$OH\cdot CH(CH_2\cdot O\cdot C_6H_4\cdot CO_2H)_2.$$

The free acid, m. p. 167°, crystallises from dilute alcohol in aggregates of white needles. It is not decomposed by boiling with aqueous acids or alkalis. G. T. M.

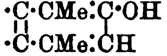
Polymerisation of Ethyl Phenylpropiolate. Paul Pfeiffer and W. Möller (*Ber.*, 1907, **40**, 3839—3844. Compare Stobbe, this vol., i, 769).—Ethyl phenylpropiolate is converted when heated in a sealed tube at 210° for ten to twelve hours into *diethyl* 1-*phenylnaphthalene*-2 : 3-*dicarboxylate*, m. p. 127—128°, identical with the compound described wrongly by Lanser as triethyl triphenyltrimesate (Abstr., 1899, i, 916). Only one of the carbethoxy-groups is hydrolysed by an aqueous or alcoholic solution of potassium hydroxide; the *ester acid*, m. p. 202—203°, so formed, probably has the formula



$C_6H_4{<}\begin{array}{l}CPh{:}C\cdot CO_2Et\\ CH{=}C\cdot CO_2H\end{array}$,

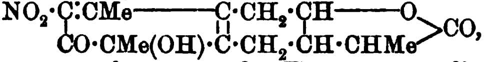
and is identical with the compound wrongly described by Lanser and Halversen (Abstr., 1902, i, 458) as monoethyl diphenyltetrenecarboxylate. It crystallises with $4H_2O$, which are driven off on heating the substance; the *sodium* salt, $C_{20}H_{15}O_4Na,6H_2O$, crystallises in small, silvery leaflets; the *calcium* salt, $(C_{20}H_{15}O_4)_2Ca$, forms small, slender needles; the *pyridinium* salt, $C_{20}H_{15}O_4,C_5H_5NH$, forms brilliant, quadratic plates, m. p. 150—152°. A mixture of the calcium salt and calcium hydroxide yields, on distillation at 325°, a substance which crystallises in brilliant, brownish-yellow needles, m. p. 157°, and is probably all*ochrysoketone* (compare Stobbe, this vol., i, 765). W. H. G.

ψ-Quinol Derivatives of the Santonin Group. Guido Bargellini (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 262—265).—Since the desmotroposantonins and the santonous acids contain the same ring,



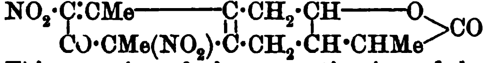
$\begin{array}{l}\cdot C\cdot CMe{:}C\cdot OH\\ \cdot C\cdot CMe{:}CH\end{array}$,

as is present in 1 : 4-dimethyl-β-naphthol, the author has investigated the oxidation of these compounds to ascertain if they also yield derivatives of the ψ-quinol type (compare this vol., i, 914). Desmotroposantonous acid gives a ψ-quinol which is apparently isomeric with santoninic acid and yields an azo-compound when treated with phenylhydrazine. From desmotroposantonin has been prepared, not the corresponding ψ-quinol or hydroxysantonin, but its nitro-derivative which was obtained by Andreocci (Abstr., 1898, i, 266), and to which the author assigns the structure



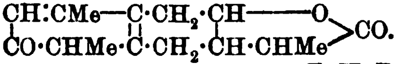
$$\begin{array}{l}NO_2\cdot C{:}CMe\text{———}C\cdot CH_2\cdot CH\text{——}O\\ CO\cdot CMe(OH)\cdot C\cdot CH_2\cdot CH\cdot CHMe\end{array}{>}CO,$$

as it forms an acetyl compound. The corresponding quinitrole,



$\begin{array}{l}NO_2\cdot C{:}CMe\text{———}C\cdot CH_2\cdot CH\text{——}O\\ CO\cdot CMe(NO_2)\cdot C\cdot CH_2\cdot CH\cdot CHMe\end{array}{>}CO$,

has also been prepared. This capacity of the aromatic ring of desmotroposantonin and desmotroposantonous acid of becoming alicyclic in the transformation of these compounds into ψ-quinols would indicate that the type changes from that of desmotroposantonin to that of santonin, and that the latter should have the formula:



$\begin{array}{l}CH{:}CMe\text{—}C\cdot CH_2\cdot CH\text{——}O\\ CO\cdot CHMe\cdot C\cdot CH_2\cdot CH\cdot CHMe\end{array}{>}CO.$

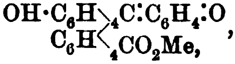
T. H. P.

Constitution of Phthalein Salts. RICHARD MEYER and KARL MARX (*Ber.*, 1907, 40, 3603—3605).—An intensely yellow *diethyl* quinonoid derivative of phenolphthalein, m. p. 98—104°, similar to the quinonoid derivative of tetrabromophenolphthalein (this vol., i, 421), has been prepared by the action of ethyl iodide on the solid potassium salt; on recrystallisation, it is transformed into the stable lactone ether, m. p. 118—120°.

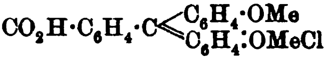
The absorption spectra of the alkali salts of phenolphthalein, quinolphthalein, and fluorescein are compared. If the wave-lengths of the absorbed light are taken as a function of the concentration of the solutions, the three spectra give similar curves. That the curve for fluorescein, although differing in position, is similar in shape to those for phenolphthalein and quinolphthalein, which lie close together, shows that the difference between these three substances is one of degree and not fundamental. G. Y.

Halochromism of Phenolphthalein and its Esters. KURT H. MEYER and ARTHUR HANTZSCH (*Ber.*, 1907, 40, 3479—3488).—Whilst the behaviour of phenolphthalein towards alkalis and the constitution of its alkali salts have been frequently investigated, its basic properties and its power of forming salts with acids have been comparatively little studied. The authors have accordingly found that phenolphthalein forms a red salt with hydrogen chloride at - 30°, but the salt could not be isolated; on the other hand, brilliant red compounds were obtained with aluminium chloride and stannic chloride respectively. The lactoid dimethyl ether of phenolphthalein exhibits a similar behaviour towards these chlorides.

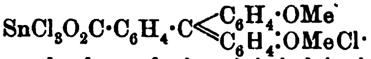
The authors confirm the results of Green and King (Abstr., 1906, i, 670) with regard to the quinonoid methyl ester of phenolphthalein and agree with their theoretical conclusions. This compound also forms double salts. Since the alkali salts of phenolphthalein have the same colour as those of the quinonoid ester, the quinonoid formula is assigned to the former. The following formulæ are accordingly submitted:



$$\begin{matrix}\mathrm{OH{\cdot}C_6H_4}\\ \mathrm{CO_2Me{\cdot}C_6H_4}\end{matrix}\!>\mathrm{C{:}C_6H_4{:}O},$$

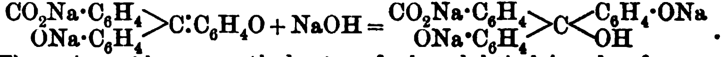


$$\mathrm{CO_2H{\cdot}C_6H_4{\cdot}C}\!<\!\begin{matrix}\mathrm{C_6H_4{\cdot}OMe}\\ \mathrm{C_6H_4{:}OMeCl}\end{matrix}$$



$$\mathrm{SnCl_3O_2C{\cdot}C_6H_4{\cdot}C}\!<\!\begin{matrix}\mathrm{C_6H_4{\cdot}OMe}\\ \mathrm{C_6H_4{:}OMeCl}\end{matrix}.$$

The fact that the red colour of phenolphthalein in alkaline solution is discharged by excess of alkali is not due to the formation of the colourless sodium salt of phenolphthalein, as is often supposed; the decolorisation is a time phenomenon and is formulated as follows:

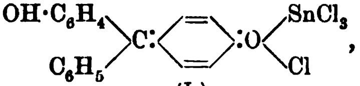


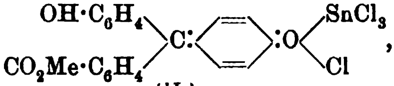
$$\begin{matrix}\mathrm{CO_2Na{\cdot}C_6H_4}\\ \mathrm{ONa{\cdot}C_6H_4}\end{matrix}\!>\mathrm{C{:}C_6H_4O}+\mathrm{NaOH}=\begin{matrix}\mathrm{CO_2Na{\cdot}C_6H_4}\\ \mathrm{ONa{\cdot}C_6H_4}\end{matrix}\!>\mathrm{C}\!<\!\begin{matrix}\mathrm{C_6H_4{\cdot}ONa}\\ \mathrm{OH}\end{matrix}.$$

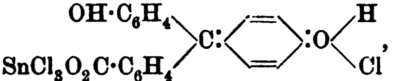
The quinonoid monomethyl ester of phenolphthalein also forms red double salts with stannic chloride and aluminium chloride; these salts are undoubtedly of quinonoid structure.

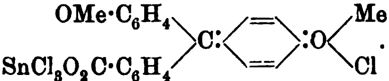
The double salts of phenolphthalein and its lactoid dimethyl ether have, not only the same colour when solid, namely, cinnabar-red, but in solution have almost the same absorption spectra as the salts of the quinonoid ester, exhibiting a characteristic green band. The conclusion is drawn that the salts of the lactoid ether are quinonoid, in fact, *all salts of phenolphthalein with acids are quinonoid.*

The tin double salts of benzaurin (I), the quinonoid ester (II), phenolphthalein (III), and the lactoid dimethyl ether (IV) are respectively represented as follows:


(I.)


(II.)


(III.)


(IV.)

When hydrogen chloride is passed over dry phenolphthalein at the ordinary temperature, there is no change, but at −30° addition of from 1—2 mols. of the acid takes place, the salt being red; on rise of temperature, however, all the hydrogen chloride is eliminated.

The *salt*, $C_{20}H_{14}O_4,AlCl_3$, obtained by adding the calculated amount of a solution of aluminium chloride in nitrobenzene to a solution of phenolphthalein in nitrobenzene and then pouring the mixture into carbon disulphide, is a cinnabar-red powder, which chars on being heated. The *salt*, $C_{20}H_{14}O_4,C_6H_5{\cdot}NO_2,SnCl_4$, obtained from stannic chloride in a similar manner, is a red, hygroscopic powder. The *salt*, $C_{22}H_{18}O_4,AlCl_3$, obtained from the lactoid dimethyl ether, is a cinnabar-red powder. The *salt*, $C_{22}H_{18}O_4,SnCl_4$, forms red crystals, m. p. 128—129°; its solution in chloroform is red; its alcoholic solution orange-yellow.

Quinonoid phenolphthalein methyl ester (methyl benzaurin-carboxylate), obtained by the action of methyl sulphate on phenolphthalein (compare Green and King, *loc. cit.*), is a red, amorphous powder melting indefinitely between 127° and 130°. Its concentrated solutions are red, but become yellow on dilution; its solution in liquid ammonia in reddish-violet. It undergoes saponification with great ease. It forms the *salt*, $C_{21}H_{16}O_4,AlCl_3$, which is a cinnabar-red powder. The *salt*, $C_{21}H_{16}O_4,SnCl_4$, forms red flakes.

The absorption spectra of the tin-double salts prepared are described.

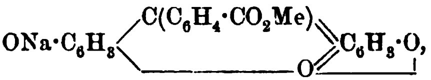
The red solutions of phenolphthalein alkali salts require such a large excess of alkali in order to be decolorised that the reaction cannot be clearly followed by conductivity measurements. Tetrabromophenolphthalein was, however, examined from this standpoint. A. McK.

Constitution of the Phenolphthalein and Quinolphthalein Salts. II. ARTHUR G. GREEN and PERCY E. KING (*Ber.*, 1907, **40**, 3724—3734. Compare Abstr., 1906, i, 670*).—The scarlet compound described previously as the quinonoid methyl ester of phenolphthalein is found to be the hydrochloride of the ester. The *ester*, which is much

* See also Proc., 1907, **23**, 228.

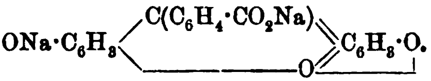
more stable than its hydrochloride, is obtained best by passing dry hydrogen chloride into a solution of phenolphthalein in methyl alcohol and 100% sulphuric acid, and, after keeping overnight, pouring the solution into ammonium hydroxide at 0°. After purification, it crystallises in orange, prismatic needles, and in alcoholic solution yields with hydrochloric acid a scarlet solution of the chloride which gradually loses its colour and yields phenolphthalein. The ester forms a violet-red solution in alkali hydroxides, from which the unchanged methyl ester is obtained by immediate acidification and phenolphthalein by postponed acidification. The methyl ester of quinolphthalein in the form of its chloride exhibits precisely analogous behaviour, and forms a bluish-purple solution in alkalis.

For these coloured alkali salts of the esters, the authors recommend the formulæ: $ONa\cdot C_6H_4\cdot C(C_6H_4\cdot CO_2Me)\colon C_6H_4\colon O<^{H}_{OH}$ and



$$ONa\cdot C_6H_3\left\langle\begin{matrix}C(C_6H_4\cdot CO_2Me)\\ O\end{matrix}\right\rangle C_6H_3\cdot O,$$

and from analogy the coloured salts of phenol- and of quinol-phthaleins must be represented by $ONa\cdot C_6H_4\cdot C(C_6H_4\cdot CO_2Na)\colon C_6H_4\colon O<^{H}_{OH}$ and



$$ONa\cdot C_6H_3\left\langle\begin{matrix}C(C_6H_4\cdot CO_2Na)\\ O\end{matrix}\right\rangle C_6H_3\cdot O.$$

These conclusions, which accord with the behaviour of the salts of the phthaleins and their esters with excess of potassium hydroxide and with alcohol, the salts of the esters remaining coloured, are confirmed by a study of the lactonoid methyl and dimethyl ethers of phenolphthalein and quinolphthalein (Meyer and Spengler, Abstr., 1905, i, 440). The methyl ethers represented by the preceding quinonoid structures would not contain a phenolic hydroxyl group, and consequently should not form coloured alkali salts, and should yield esters insoluble in alkalis. This is actually the case. Phenolphthalein methyl ether has a double m. p. initially at 148—149°, and after resolidification at 80°; in alkalis, it yields a faintly red solution, the colour of which is weaker the purer the ether (Meyer and Spengler: m. p. 141—142°, red solution in alkalis). This solution probably contains the colourless carbinol salt,

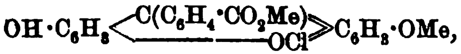
$$OMe\cdot C_6H_4\cdot C(OH)(C_6H_4\cdot CO_2Na)\cdot C_6H_4\cdot OH.$$

Quinolphthalein methyl ether separates from benzene in colourless prisms, m. p. 118—122°, and after removal of the benzene of crystallisation, m. p. 107—109°; it dissolves in alkalis forming a colourless solution of the carbinol salt (compare Nietzki and Burckhardt, Abstr., 1897, i, 225).

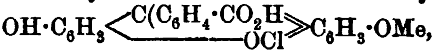
The *methyl ester* of *phenolphthalein methyl ether*,

$$OMe\cdot C_6H_4\cdot C(C_6H_4\cdot CO_2Me)\colon C_6H_4\colon O,$$

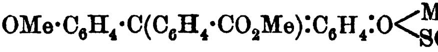
obtained from the lactonoid methyl ether in a similar manner to the methyl ester of phenolphthalein, is an orange substance insoluble in alkalis; the hydrolysed compound yields the original lactonoid ether by acidification. The *methyl* ester of *quinolphthalein methyl ether* is obtained in the form of the *chloride*,



$$\mathrm{OH{\cdot}C_6H_3}<\!\genfrac{}{}{0pt}{}{\mathrm{C(C_6H_4{\cdot}CO_2Me)}}{\mathrm{OCl}}\!>\mathrm{C_6H_3{\cdot}OMe},$$

when dry hydrogen chloride is passed into a methyl-alcoholic solution of the lactonoid ether; it forms red plates, readily loses methyl chloride, is insoluble in aqueous alkalis, and yields the lactonoid ether by hydrolysis. The *chloride*,  $\mathrm{OH{\cdot}C_6H_3}<\!\genfrac{}{}{0pt}{}{\mathrm{C(C_6H_4{\cdot}CO_2H)}}{\mathrm{OCl}}\!>\mathrm{C_6H_3{\cdot}OMe}$, is prepared by passing hydrogen chloride into a glacial acetic acid solution of quinolphthalein methyl ether; it forms dark red, glistening crystals, and is instantaneously decomposed by water or moist ether.

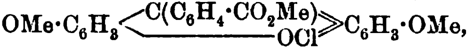
The esters of dimethylated phenol- or quinol-phthalein are obtained only in the form of salts, such as the *sulphate*,



$$\mathrm{OMe{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}CO_2Me){:}C_6H_4{:}O}<\!\genfrac{}{}{0pt}{}{\mathrm{Me}}{\mathrm{SO_4H}},$$

which is an unstable, scarlet substance. More stable is the red double salt, $\mathrm{2[OMe{\cdot}C_6H_4{\cdot}C(C_6H_4{\cdot}CO_2Me){:}C_6H_4{:}OMeCl],SnOCl_2}$, which is decolorised by water, alcohol, or alkalis with regeneration of the lactonoid ether.

The *methyl ester chloride* of *quinolphthalein dimethyl ether*,



$$\mathrm{OMe{\cdot}C_6H_3}<\!\genfrac{}{}{0pt}{}{\mathrm{C(C_6H_4{\cdot}CO_2Me)}}{\mathrm{OCl}}\!>\mathrm{C_6H_3{\cdot}OMe},$$

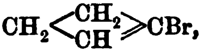
is isolated in the form of the double *salt*, $\mathrm{2C_{22}H_{19}O_5Cl,ZnCl_2}$, which is an orange-red substance. C. S.

Preparation of *o*-Carboxyphenylthioglycollic Acid. KALLE & Co. (D.R.-P. 181658).—When diazotised anthranilic acid is treated with sodium monosulphide, a poor yield of thiosalicylic and salicylic acids is obtained, but when sodium polysulphide is employed a new sulphur derivative is obtained, which, unlike thiosalicylic acid, is insoluble in alcohol, and yields *o-carboxyphenylthioglycollic acid*, $\mathrm{CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$, on treatment with an alkaline solution of sodium chloroacetate. G. T. M.

Nitration of Benzoylvanillin. JOAN POPOVICI (*Ber.*, 1907, **40**, 3504—3506).—When benzoylvanillin is nitrated by cold concentrated nitric acid, one nitro-group only enters into the ring. It takes up the ortho-position relatively to the aldehyde group; this was proved by comparing the compound obtained with that resulting from the action of benzoyl chloride on (vic-) *o*-nitrovanillin; the phenylhydrazones are also identical.

Benzoylvanillinphenylhydrazone separates from glacial acetic acid in prisms, m. p. 209—210° (corr.).

(vic-)o-*Nitrobenzoylvanillin*, $\mathrm{CHO{\cdot}C_6H_2(NO_2)(OMe){\cdot}OBz}$ (1:2:3:4), separates from glacial acetic in colourless prisms, m. p. 97°. Its *phenylhydrazone* separates from glacial acetic acid in golden-yellow plates, m. p. 192°. A. McK.

***cyclo*Butanone.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 922—925. Compare Abstr., 1905, i, 355).—Further details are given for the preparation of pure *cyclo*butanone together with fresh determinations of some physical constants. *cyclo*Butanone, b. p. 98·5—99°/745 mm.; D_0^0 0·9548; D_0^{16} 0·9382; n_D^{16} 1·4220. The semicarbazone of *cyclo*-butanone has m. p. 201° (decomp.). When boiled with lead oxide and water, 1 : 1-dibromo*cyclo*butane is converted into *cyclo*butanone and an unsaturated *bromide*, probably  $CH_2<\begin{smallmatrix}CH_2\\CH\end{smallmatrix}\gg CBr$, b. p. 93—95°. Z. K.

***cyclo*Nonanone.** Richard Willstätter and Tokuhei Kametaka (*Ber.*, 1907, **40**, 3876).—The authors confirm the observations of Zelinsky (this vol., i, 780) regarding the formation of *cyclo*nonanone from sebacic acid. A. McK.

Terpenes and Ethereal Oils. LXXXVII. Nopinone. Otto Wallach and Arnold Blumann (*Annalen*, 1907, **356**, 227—249).—Nopinone (Baeyer and Villiger, Abstr., 1896, i, 622) has been prepared previously in such small amounts that only its b. p. has been determined. It was desirable therefore to attempt the preparation of larger quantities.

Nopic acid, m. p. 126°, $[\alpha]_D$ −15·64°, is best isolated from the oxidation product of turpentine oil by conversion into its sparingly soluble sodium salt. Much better yields are obtained from dextrorotatory American than from lævorotatory French turpentine oil.

Nopinone, $C_9H_{14}O$, is obtained in good yields by adding potassium permanganate and concentrated sulphuric acid to a hot aqueous solution of sodium nopate. It solidifies in a freezing mixture to a crystalline mass, m. p. slightly above 0°, b. p. 209°, D 0·981, n_D^{20} 1·4787, $[\alpha]_D$ + 18·48° when undiluted, + 37·27°— + 38·04° in alcohol, + 11·02° in ether, or + 10·79°— + 10·95° in benzene. When treated with hydrogen chloride in alcoholic solution, it condenses, forming the *trichloride*, $C_{18}H_{29}OCl_3$, which crystallises in stout prisms, decomp. 148° (evolving gas), and on prolonged boiling in solution or digestion with 1 mol. of sodium ethoxide is converted into the *dichloride*, $C_{18}H_{28}OCl_2$, crystallising in needles, m. p. 125—126°. The trichloride is again formed on treating the dichloride with hydrogen chloride in alcoholic solution; the ease with which it is formed together with its sparing solubility makes the trichloride suitable for the recognition of nopinone. On prolonged boiling with dilute sulphuric acid, nopinone is transformed into 1-*iso*propyl-Δ^2-*cyclo*hexene-4-one (Abstr., 1906, i, 195).

Reduction of nopinone with sodium in moist ethereal solution leads to the formation of two nopinols, probably *cis*- and *trans*-isomerides. *a-Nopinol*, $C_9H_{15}\cdot OH$, sublimes in white needles, m. p. 102°, b. p. 204—205°, $[\alpha]_D$ −5·32°, remains unchanged in contact with dilute sulphuric acid, and forms a *phenylurethane*, $NHPh\cdot CO_2\cdot C_9H_{15}$, m. p. 131—132°. *β-Nopinol* is obtained as a viscid mass, $[\alpha]_D$ 15·03°, forms a *phenylurethane*, m. p. 95—96°, and when heated with zinc chloride yields a small amount of nopinonene, C_9H_{14}, b. p. 157—160°.

Reduction of nopinone by means of sodium in alcoholic solution leads to the formation of the *pinacone*, $C_{18}H_{30}O_2$, which is obtained in crystals, m. p. 106—107°, b. p. 195—200°/11 mm.

Homonopinol (*methylnopinol*, *pinene hydrate*), $C_{10}H_{17}\cdot OH$, prepared by the action of magnesium methyl iodide on nopinone, crystallises in needles, m. p. 58—59°, b. p. 204—205°, $[\alpha]_D$ −4·99°, has an odour resembling camphor, is stable towards permanganate, and yields *cis*-

terpin hydrate when shaken with 5% sulphuric acid, or in less amount when treated with cold saturated oxalic acid. The action of formic acid on homonopinol leads to the formation of a mixture of products resulting probably from the primary formation of terpin and the further transformation of this into dipentene, terpinol, terpinene, and terpineol. Dipentene dihydrochloride is formed by the action of hydrogen chloride on homonopinol in glacial acetic acid solution.

When heated with zinc chloride, homonopinol yields polymerisation products together with small amounts of hydrocarbons, which boil chiefly at 170—180°, are volatile with steam, and have an odour of limonene. The action of potassium hydrogen sulphate on homonopinol at 130° leads to the formation of a *hydrocarbon*, $C_{10}H_{16}$, b. p. 163—164°.

On treatment with phosphorus pentachloride in light petroleum, homonopinol yields a chloride, $C_{10}H_{17}Cl$, b. p. 95—105°/13 mm. or 200—205°/760 mm. evolving hydrogen chloride, which is isomeric with the chloride obtained by the action of hydrogen chloride on pinene, and on treatment with hydrogen chloride in glacial acetic acid solution yields dipentene dihydrochloride. The action of amyl nitrite and nitric acid on the chloride leads to the formation of a *nitrosate* containing chlorine; when treated with aniline, the chloride yields dipentene. This chloride may be formed as an intermediate product in the formation of dipentene by the action of hydrogen chloride on moist pinene. G. Y.

[Alkylation of ψ-Ionone.] Haarmann and Reimer (D.R.-P. 183855).—ψ-Ionone, when mixed with five parts of methyl sulphate and the solution subsequently warmed at 40°, yields an alkylated product which is separated by distillation in steam. The alkyl derivative when freed from ionone by sodium hydrogen sulphite has the following properties: b. p. 135°/12 mm., D^{20} 0·945, n_D 1·5150. It is, however, a mixture, the ketonic constituent of which when separated by means of semicarbazone has b. p. 120—128°/12 mm., D^{20} 0·940, n_D 1·491—1·494. A semicarbazide, $C_{13}H_{21}ON_3$, was obtained, m. p. 182—183°. These results point to the production of a new methylionone. G. T. M.

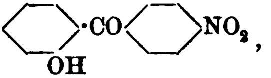
1-Chloroacetyl-2-chloro-4-aminobenzene [ω-2-Dichloro-4-aminoacetophenone] and its Derivatives. Franz Kunckell and A. Richartz (*Ber.*, 1907, 40, 3394—3397).—ω-2-*Dichloro*-4-*acetylaminoacetophenone* (3-*chloro*-4-*chloroacetylacetanilide*),

$$CH_2Cl\cdot CO\cdot C_6H_3Cl\cdot NHAc,$$

obtained by Friedel-Craft's synthesis from chloroacetyl chloride and *m*-chloroacetanilide in the presence of carbon disulphide, crystallises from benzene and melts at 146—147°.

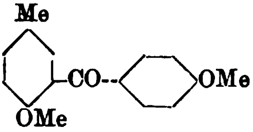
When oxidised with acidified permanganate, the ketone yields 1-*chloro*-2-*acetylaminobenzoic acid*, $C_9H_8O_3NCl$, m. p. 206—207°, and this on hydrolysis yields Tiemann's 2-chloro-4-aminobenzoic acid (Abstr., 1891, 704).

ω-2-*Dichloro*-4-*aminoacetophenone*, obtained by hydrolysing the acetyl derivative, yields a *hydrochloride*, $CH_2Cl\cdot CO\cdot C_6H_3Cl\cdot NH_2,HCl$, in the form of yellowish-red needles, m. p. 278° (decomp.). The free amine melts at 95—97°. J. J. S.

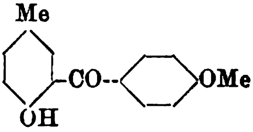
Saponifiability of Ethers of Aromatic Hydroxy-ketones. KARL AUWERS and ERICH RIETZ (*Ber.*, 1907, 40, 3514—3521).—It has been pointed out by Auwers (Abstr., 1904, i, 67) that, by the condensation of phenetole with *p*-nitrobenzoyl chloride in the presence of aluminium chloride, small amounts of 4′-nitro-2-hydroxybenzophenone, 

, are formed in addition to the normal product, 4′-nitro-4-ethoxybenzophenone. The conclusion was drawn that the ethers of aromatic *o*-hydroxyketones are more readily saponified than the isomeric para-derivatives.

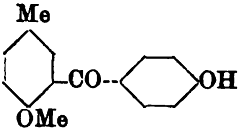
In support of this view, the authors have studied the behaviour of the ketone (I) on saponification with aluminium chloride; a mono-



(I.)



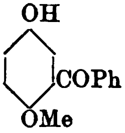
(II.)



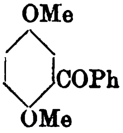
(III.)

methylated compound is formed which is not attacked by aluminium chloride even at 220°. The other methyl group, on the other hand, is eliminated with remarkable ease; in the synthesis of the dimethyl ether from *p*-cresol methyl ether and anisic chloride, the monomethyl ether is formed in about the same amount of the dimethyl ether. That the product of the partial saponification has the formula (II) was proved by the fact that the isomeric ether (III) is produced by the condensation of *p*-cresol methyl ether with *p*-nitrobenzoyl chloride and subsequent displacement of the nitro- by the hydroxy-group. The latter compound is saponified with great ease.

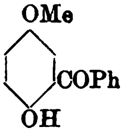
Kauffmann ascribed the formula (IV) to the substance obtained



(IV.)



(V.)



(VI.)

by the partial saponification of the compound (V). The authors conclude that the correct formula is (VI), since cryoscopic determinations in *p*-dibromobenzene solutions give normal values.

Similar results were obtained with ethers of another series of dihydroxy-ketones.

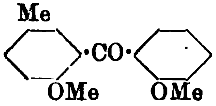
2 : 4′-*Dimethoxy*-5-*methylbenzophenone*, $C_{16}H_{16}O_3$, separates from light petroleum in colourless needles, m. p. 69—70°. 2-*Hydroxy*-4′-*methoxy*-5-*methylbenzophenone*, $C_{15}H_{14}O_3$, separates from dilute alcohol in yellow leaflets, m. p. 108—109°. Its *dibromo*-derivative, $C_{15}H_{12}O_3Br_2$, crystallises from glacial acetic acid in yellow needles, m. p. 168—169°.

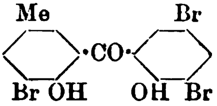
4′-*Nitro*-2-*methoxy*-5-*methylbenzophenone*, $C_{15}H_{13}O_4N$, separates from light petroleum in golden, glistening leaflets, m. p. 101—102°.

4′-Amino-2-methoxy-5-methylbenzophenone, $C_{15}H_{15}O_2N$, obtained by the reduction of the preceding compound with ammonium sulphide, separates from benzene in tiny needles, m. p. 152°. *4′-Amino-2-hydroxy-5-methylbenzophenone*, $C_{14}H_{13}O_2N$, separates from dilute acetic acid in leaflets, m. p. 137°.

4′-Hydroxy-2-methoxy-5-methylbenzophenone, $C_{15}H_{14}O_3$, obtained from 4′-amino-2-methoxy-5-methylbenzophenone by replacing the amino- by the hydroxy-group, crystallises from benzene in glistening leaflets, m. p. 160°. When saponified, it forms 2 : *4′-dihydroxy-5-methylbenzophenone*, $C_{14}H_{12}O_3$, which crystallises from benzene in tiny, yellow needles, m. p. 150—151°. The latter compound forms a *tribromo*-derivative, $C_{14}H_9O_3Br_3$, crystallising from glacial acetic acid in yellow needles, m. p. 211·5—202·5°.

The ketone (VII), obtained from *o*-methoxybenzoyl chloride and


(VII.)


(VIII.)

p-cresol methyl ether, was saponified at 100° with aluminium chloride and the product brominated, when the *tribromo*-compound (VIII) was obtained; it separates from glacial acetic acid in yellow crystals, melting indefinitely at 190°. A. McK.

Dinitro- and Dibromo-2 : 2′-dihydroxydibenzylideneacetone.

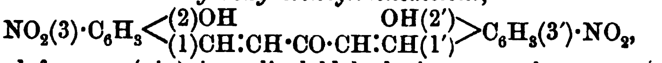
RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1907, **40**, 3455—3461).—Compounds of the types CHR:CH·CO·CH:CHR and

CHR:CH·CO·CH:CHR′

have already been studied by Claisen and others; the authors have been interested in the effect of the substitution of nitro- or bromine groups on the behaviour as dyes of those types which possess the complex chromophore C:C·CO·C:C, are symmetrically constituted, and in which the two hydrogen atoms in the ortho-positions in each ring are substituted by hydroxyl groups.

It has been previously shown by Fabinyi (D.R.-P. 110521) that salicylaldehyde and acetone interact in alcoholic solution in the presence of concentrated sodium hydroxide to form the sodium salt of 2 : 2′-dihydroxydibenzylideneacetone, from which the latter compound itself is isolated when dilute mineral acid is added.

3 : *3′-Dinitro-2 : 2′-dihydroxydibenzylideneacetone*,



$$NO_2(3)\cdot C_6H_3<\begin{matrix}(2)OH \qquad\qquad\qquad\qquad OH(2') \\ (1)CH{:}CH\cdot CO\cdot CH{:}CH(1')\end{matrix}>C_6H_3(3')\cdot NO_2,$$

obtained from *m*-(*vic*-)nitrosalicylaldehyde in an analogous manner, separates from alcohol in yellow needles, m. p. 231—232° (decomp.). Its solution in concentrated sulphuric acid is yellowish-red and becomes colourless on the addition of water. The sodium salt forms glistening ruby-red crystals. The *diacetyl* derivative separates from glacial acetic acid in yellow crystals, m. p. 228—230° (decomp.); the *dibenzoyl* derivative separates from nitrobenzene in tiny, yellow crystals, m. p. 235—238° (decomp.).

5 : 5′-*Dinitro*-2 : 2′-*dihydroxydibenzylideneacetone*, obtained from *m*-(*as*-)nitrosalicylaldehyde, separates from alcohol in orange-yellow crystals, m. p. 212—214° (decomp.); its solution in concentrated sulphuric acid is orange-red; its sodium salt is reddish-brown. Its *diacetyl* derivative separates from glacial acetic acid in yellow scales, m. p. 203°.

4 : 4′-*Dinitro*-2 : 2′-*dihydroxydibenzylideneacetone*, obtained by the direct nitration of 2 : 2′-dihydroxydibenzylideneacetone, separates from alcohol in tiny needles, m. p. about 204° (decomp.); its solution in concentrated sulphuric acid is orange-red; its solution in alkali, cherry-red; its sodium salt is dark red. Its *diacetyl* derivative separates from glacial acetic acid in tiny leaflets, m. p. 196° (decomp.).

By the action of concentrated nitric acid on 2 : 2′-dihydroxydibenzylideneacetone, the more highly nitrated compound, *tetranitro*-2 : 2′-*dihydroxydibenzylideneacetone*, $CO[CH{:}CH{\cdot}C_6H_2(NO_2)_2{\cdot}OH]_2$, may be obtained under the conditions quoted; it separates from nitrobenzene in yellow needles; its solution in concentrated sulphuric acid is orange-coloured; it begins to decompose at 240°.

5 : 5′-*Dibromo*-2 : 2′-*dihydroxydibenzylideneacetone*, obtained from 5-bromosalicylaldehyde, crystallises from alcohol in yellow needles, m. p. 188° (decomp.); its solution in dilute aqueous sodium hydroxide is red, and the sodium salt is reddish-brown. Its solution in concentrated sulphuric acid is cherry-red; its solution in concentrated aqueous sodium hydroxide is bluish-violet. Its *diacetyl* derivative crystallises from glacial acetic acid in tiny, yellow needles, m. p. 187—188° (decomp.). The *dimethoxy*-derivative, obtained by the action of methyl iodide on the sodium salt, crystallises from alcohol in yellow leaflets, m. p. 137°; the *diethoxy*-derivative forms yellow leaflets, m. p. 131°. The *dibenzoyl* derivative crystallises from benzene in yellow crystals, m. p. 221° (decomp.).

2 : 2′-*Diacetoxydibenzylideneacetone* crystallises from glacial acetic acid or alcohol in yellow needles, m. p. 128°. 2 : 2′-*Dimethoxydibenzylideneacetone* separates from alcohol in glistening yellow leaflets, m. p. 124°. 2 : 2′-*Diethoxydibenzylideneacetone* forms glistening yellow leaflets, m. p. 89°. 2 : 2′-*Dibenzoyloxydibenzylideneacetone* forms yellowish-white crystals, m. p. 135°. A. McK.

Duplobenzylidenethioacetone and the Oxonium Theory. HANS VON LIEBIG (*J. pr. Chem.*, 1907, [ii], 76, 277—280).—A criticism of Fromm and Höller's views as the constitution of the additive compounds of duplobenzylidenethioacetone (this vol., i, 710) from the standpoint of the present author's view of the nature of oxonium salts (this vol., i, 45). G. Y.

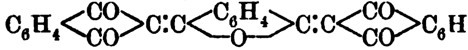
Acetalation of Aldehydes and Ketones. LUDWIG CLAISEN (*Ber.*, 1907, 40, 3903—3914).—In consequence of the criticisms of many investigators, the author publishes the details of his process for obtaining acetals in nearly quantitative yield from aldehydes or ketones by means of ethyl orthoformate. The aldehyde, or ketone (1 mol.), and ethyl orthoformate (1·1 mols.) are dissolved in alcohol (not less than 3 mols.) and the mixture, in the presence of a catalyst, such as a mineral acid, ferric chloride, or ammonium chloride, is kept at the ordinary temperature or is gently warmed.

o-Ethers of β-diketones and of the esters of ketonic acids are also obtained by this method. Benzoylacetone yields the *ether*, $COPh\cdot CH\colon CMe\cdot OEt$, b. p. 162—164°, D^{15} 1·058, which is converted by hydroxylamine into 3-*phenyl*-5-*methyl*iso*oxazole*, m. p. 42—43°.

If too large a quantity of the catalyst is used in the process, or if the time is unduly prolonged, the yield of the acetal may diminish to zero.

Arbusoff's experiments on the acetalation of acetone and acetophenone by ethyl orthoformate and alcohol without a catalyst (this vol., i, 749) have been repeated, and not a trace of the acetal has been obtained. C. S.

Condensation of Diketohydrindene [1 : 3-Indandione] with Phthalic Anhydride. CARMELO MARCHESE (*Gazzetta*, 1907, 37, ii, 303—309).—*Anhydrophthalylbis*-1 : 3-*indandione*,

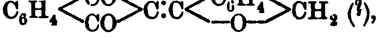


$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C{:}C{<}\begin{matrix}C_6H_4\\O\end{matrix}{>}C{:}C{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4,$$

prepared by the condensation of phthalic anhydride with 1 : 3-indandione or ethyl 2-sodio-1 : 3-diketohydrindene-2-carboxylate in presence of acetic anhydride, crystallises from xylene or nitrobenzene in yellow needles, m. p. 325°, and dissolves in alkali hydroxides, giving intensely red solutions.

Phthalylbis-1 : 3-*indandione*, $C_6H_4[CO\cdot CH\colon(CO)_2\colon C_6H_4]_2$, obtained by boiling the preceding compound with alcoholic potassium hydroxide solution, separates from ethyl acetate in faintly yellow, shining crystals, m. p. 198°, and dissolves readily in nitrobenzene and sparingly in alcohol, benzene, xylene, or acetic acid. The salts of the alkali metals and of calcium are intensely red and readily soluble in water; the *barium* salt, $C_{26}H_{12}O_6Ba,11H_2O$, was analysed.

Reduction of anhydrophthalylbis-1 : 3-indandione by means of zinc dust and acetic acid yields the *compound*,



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C{:}C{<}\begin{matrix}C_6H_4\\O\end{matrix}{>}CH_2\ (?),$$

m. p. 275°, which dissolves in acetic acid or ethyl acetate and, to a slight extent, in alcohol, water, benzene, or xylene.

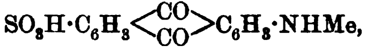
An attempt to condense camphoric anhydride with 1 : 3-indandione in presence of acetic anhydride yielded 2-acetyl-1 : 3-indandione (compare Schwerin, Abstr., 1894, i, 194). T. H. P.

New Anthraquinone Derivatives. EDUARD LAUBÉ (*Ber.*, 1907, 40, 3562—3567).—1-p-*Bromoanilinoanthraquinone*, prepared by condensing aminoanthraquinone with *p*-dibromobenzene in presence of potassium carbonate and copper powder, is a dark red powder, m. p. 308°, dissolving in concentrated sulphuric acid with a green coloration which changes to a scarlet-red on the addition of a drop of dichromate. p-*Phenylenebis*-1-*aminoanthraquinone*, obtained at the same time as the above compound, separates from chloroform as a blackish-violet powder giving a violet, metallic, glistening mark on porcelain, m. p. above 320°. 2-p-*Bromoanilinoanthraquinone* forms ball-like, scarlet-red crystals, m. p. 242°, dissolving in sulphuric acid with a cornflower-blue coloration. p-*Phenylenebis*-2-*aminoanthraquinone* is a dark brown powder, m. p. 300°, giving a greenish-blue coloration with sulphuric acid.

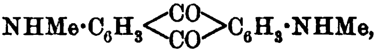
1-Iodoanthraquinone reacts more easily with carbazole and with diphenylamine than the corresponding chloro-compound. N-*Anthraquinonylcarbazole* crystallises in well-formed, ruby-red crystals, m. p. 252—254°, dissolving in sulphuric acid with an emerald-green coloration which, on warming, changes through olive-green to brown. It gives rise to a yellowish-red solution with green fluorescence when reduced with zinc and acetic acid. 1-*Diphenylaminoanthraquinone* is a blackish-red powder, dissolving with an olive-green coloration in sulphuric acid. E. F. A.

[Preparation of Amino-, Alkylamino-, and Arylamino-derivatives of Anthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 181722. Compare this vol., i, 224).—The sulphonic groups in 1 : 5- and 1 : 8-anthraquinonedisulphonic acids may be partially or completely replaced by amino-, alkylamino-, or arylamino-groups by heating the alkali salts of these acids with ammonia, an alkylamine, or an aromatic amine.

1-*Methylaminoanthraquinone*-5-*sulphonic acid*,



$$\mathrm{SO_3H\cdot C_6H_3}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{C_6H_3\cdot NHMe},$$

is produced together with a small amount of *s*-dimethyl-1 : 5-diaminoanthraquinone,  $\mathrm{NHMe\cdot C_6H_3}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{C_6H_3\cdot NHMe}$, by heating potassium 1 : 5-anthraquinonedisulphonate with aqueous methylamine at 150°; the *potassium* salt crystallises from water in violet-brown needles.

1-*Methylaminoanthraquinone*-8-*sulphonic acid*, 1-*aminoanthraquinone*-5-*sulphonic acid*, and 1-*aminoanthraquinone*-8-*sulphonic acid* are similarly obtained, and their tinctorial properties are described in the patent.

s-1 : 5-*p*-Ditolylaminoanthraquinone may be prepared from 1 : 5-anthraquinonedisulphonic acid and *p*-toluidine. G. T. M.

Preparation of Trichloroanthraflavic Acid. R. WEDEKIND (D.R.-P. 181659).—The chlorine additive product of anthraflavic acid ("hexachloroanthraflavic acid"), when heated with phenol or some other solvent of high boiling point, such as xylene or nitrobenzene, loses hydrogen chloride and furnishes a *trichloroanthraflavic acid*, which separates in lustrous, yellow needles. This compound, which is employed in the preparation of dyes of the anthracene series, is insoluble in water, and yields a sparingly soluble *sodium* salt.

G. T. M.

Preparation of Dianthraquinonyl and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 184495).—The following is an alternative method of preparing dianthraquinonyl and its derivatives. 1-Amino-2-methylanthraquinone is diazotised in sulphuric acid and the dry diazo-sulphate suspended in acetic anhydride and treated with copper powder, when 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl is obtained (compare this vol., i, 539). G. T. M.

Preparation of a Chlorine Additive Compound of Anthraflavic Acid. R. WEDEKIND (D.R.-P. 179916).—Anthraflavic acid does not absorb chlorine in acidified water at 100°, but, when the boiling temperature is raised by the addition of sulphuric acid, substitution occurs with the formation of the dichloro-derivatives; when, however, this acid is suspended in concentrated calcium or magnesium chloride solution and treated at 110° with a mixture of sodium chlorate and hydrochloric acid, a yellow substance having the composition of a *hexachlorodihydroxyanthraquinone* is obtained. This compound is moderately stable towards acids, but is decomposed by aniline and dilute alkalis. When heated in phenol or cresol, this additive product loses hydrogen chloride and a well-defined trichloroanthraflavic acid is produced. G. T. M.

Benzanthrone Derivatives of the Naphthanthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 181176. Compare Abstr., 1906, i, 889, and this vol., i, 324).—Naphthanthraquinone resembles anthraquinone in reacting with glycerol to yield benzanthrone derivatives, which on heating with alkali hydroxides furnish blue colouring matters suitable for vat dyeing.

Benzonaphthanthrone, $C_{21}H_{12}O$, m. p. 186—188°, was prepared in the following ways: (1) by heating naphthanthraquinone with glycerol, aniline sulphate, and concentrated sulphuric acid at 150°, or by warming its dihydro-derivative with these reagents at 110°; (2) by heating the quinone or naphthanthranol with glycerol and zinc chloride at 200 to 210°. G. T. M.

Linalool is a Tertiary Alcohol. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1907, ii, 464; from *Wiss. u. ind. Ber. Roure-Bertrand Fils*, [ii], 5, 3—5).—Experiments on the formation of esters of geraniol and linalool have shown that linalool is a tertiary alcohol. The alcohols were mixed with acetic acid (6 mols.) and kept at a constant temperature. The quantities which had entered into combination after different periods are given below:

	hours.		days.					months.	
	6.	24.	3.	10.	15.	24.	45.	5.	12.
Geraniol ……	2·7	5·5	12·6	29·2	35·7	45·0	62·3	85·6	90·0%
Linalool ……	—	0·4	—	0·6	—	1·1	—	3·9	5·3%

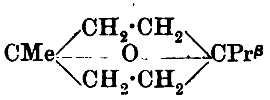
E. W. W.

Terpenes and Ethereal Oils. LXXXVI. Compounds of the Terpinene Series. OTTO WALLACH and FRIEDRICH BOEDECKER [and, in part, FRITZ MEISTER] (*Annalen*, 1907, **356**, 197—226. Compare this vol., i, 64).—This paper contains a further account of the compounds of the terpinene series and their relationships to other terpenes. Part of the details have been already published (this vol., i, 227, 228, 229); the following are new.

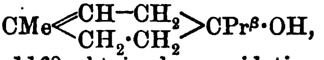
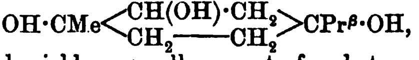
In addition to the methods of preparation described previously, terpinene dihydrochloride, m. p. 52°, has now been formed from terpineneterpin, from the saturated alcohol, $C_{10}H_{17}{\cdot}OH$, from sabinene hydrate, and from the monohydrochloride.

Terpinene monohydrochloride, $C_{10}H_{17}Cl$, b. p. 85—95°/11 mm., prepared by the action of hydrogen chloride on the terpinene in carbon disulphide solution, forms the dihydrochloride when treated with hydrogen chloride in glacial acetic acid. The monohydrochloride obtained from sabinene (this vol., i, 229) does not solidify in a mixture of solid carbon dioxide and ether, and is more stable towards potassium hydroxide than is limonene monohydrochloride.

The terpin, *terpineneterpin*, $C_{10}H_{18}(OH)_2$ (this vol., i, 229), is prepared by shaking thujene or terpineol with sulphuric acid. Terpineol is formed as an intermediate product in the preparation of the terpin from sabinene. The terpin crystallises and sublimes in white leaflets, m. p. 137—138°, b. p. 250° (slight decomp.), is markedly volatile with steam, is more readily soluble than *cis*-terpin hydrate, forms mixed crystals, m. p. about 108°, with anhydrous *cis*-terpin, and with hydrogen chloride in glacial acetic acid forms terpinene dihydrochloride.

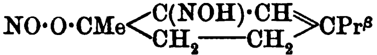


When distilled with a saturated solution of oxalic acid, terpineneterpin yields terpineol and *terpinenecineol*, which is obtained as a colourless oil, b. p. 172—173°, D 0·897, n_D 1·4485, has an odour resembling cineol, does not solidify in a mixture of solid carbon dioxide and ether, and is volatile with steam. On treatment with hydrogen bromide in light petroleum solution, it forms terpinene dihydrobromide, gives a light red, crystalline precipitate with bromine in light petroleum, and on oxidation yields products different from those obtained from cineol.

The terpineol obtained from cardamom and majorana oils must have the constitution  $\mathrm{CMe}<\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}>\mathrm{CPr^{\beta}{\cdot}OH}$, since the trihydroxyterpane, m. p. 114—116°, obtained on oxidation with potassium permanganate, yields carvenone when heated with hydrochloric acid. The trihydroxyterpane,  $\mathrm{OH{\cdot}CMe}<\begin{matrix}\mathrm{CH(OH){\cdot}CH_2}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}>\mathrm{CPr^{\beta}{\cdot}OH}$, on oxidation with chromic acid, yields a small amount of a ketone which forms a semicarbazone, $C_{10}H_{19}ON_3$, m. p. 146°, and may be thujaketone. The trihydroxyterpane is oxidised by potassium permanganate in alkaline solution, forming two isomeric acids. The *acid*, $C_{10}H_{18}O_6$, m. p. 205—206°, which is the main product, loses water when heated or when boiled with acids, forming a *lactone*, $C_{10}H_{14}O_4$, m. p. 63—64°. This is volatile with steam, and on treatment with alkalis again forms the acid, m. p. 205—206°. The isomeric *acid*, m. p. 188—189°, yields a *lactone*, $C_{10}H_{14}O_4$, m. p. 72—73°, from which it is regenerated by the action of alkalis.

The terpineol from sabinene has $[\alpha]_D$ +25°4′, and on oxidation yields a trihydroxyterpane, $[\alpha]_D$ +21°21′. Optically inactive terpineol, which on oxidation yields the acid, m. p. 188—189°, is obtained from terpinene dihydrochloride and from the fractions of commercial terpineol boiling at low temperatures. The terpineol from terpineneterpin is oxidised to the acid, m. p. 188—189°, and probably contains small amounts of Δ^4-menthene-1·ol together with the Δ^1-menthene-4-ol.

The reduction of terpinene nitrosite in alkaline solution leads to the formation of a mixture of carvenone and tetrahydrocarvenone (compare Wallach and Laufler, Abstr., 1901, i, 89; Amenomiya, Abstr., 1905, i, 603). The constitutional formula



$$NO\cdot O\cdot CMe{<}\begin{matrix}C(NOH)\cdot CH\\ CH_2\text{——}CH_2\end{matrix}{>}CPr^{\beta}$$

is ascribed to the nitrosite, which, however, in view of its chemical behaviour and in spite of the results of molecular weight determinations, is considered to be bimolecular.

The paper concludes with a discussion of the constitution of terpinene. G. Y.

Sesquiterpenes. I. Caryophyllene. Ernst Deussen and Arnold Lewinsohn (*Annalen*, 1907, **356**, 1—23).—A study of caryophyllene was undertaken in continuation of the investigation of West Indian sandalwood oil (Abstr., 1900, ii, 579; 1902, i, 552).

Caryophyllene nitrosochloride (m. p. 161—163°: Wallach and Walker, Abstr., 1893, i, 101; 158—160°: Schreiner and Kremers, Abstr., 1900, i, 106) is found to be a mixture; on extraction with alcohol containing 10% of ethyl acetate, α-caryophyllene nitrosochloride remains unchanged, and on recrystallisation from chloroform separates in glistening crystals, m. p. 177° if slowly or 179° if quickly heated; it is optically inactive, is stable, remaining unchanged when boiled with concentrated hydrochloric or nitric acids, and forms solutions in chloroform and benzene which are colourless at the ordinary temperature and become blue when heated. The alcohol-ethyl acetate extract contains β-caryophyllene nitrosochloride, which crystallises in needles, m. p. 159°, $[\alpha]_D$ −98·07°, is moderately soluble in hot light petroleum, and may be bimolecular, and a *substance*, $C_{15}H_{23}O_2N$, which crystallises in prismatic needles, m. p. 162·5—163·5°, $[\alpha]_D$ +217·2°, is sparingly soluble in light petroleum, and decolorises bromine, but does not react with benzylamine. α-Caryophyllene nitrosochloride reacts with benzylamine forming Schreiner and Kremers' β-base, m. p. 126—128° (*loc. cit.*), which therefore is α-caryophyllenenitrolbenzylamine. The *hydrochloride*, $NO\cdot C_{15}H_{24}\cdot NH\cdot CH_2Ph,HCl$, crystallises in glistening leaflets, m. p. 195°, and is optically inactive. β-Caryophyllenenitrolbenzylamine, Schreiner and Kremers' α-base, m. p. 167°, is formed by the action of benzylamine on the β-nitrosochloride; it crystallises from chloroform and alcohol in needles, m. p. 172—173°, $[\alpha]_D^{16}$ +217·87°, and yields a lævorotatory *hydrochloride*.

α-*Nitrosocaryophyllene*, $C_{15}H_{23}ON$, formed by reducing the α-nitrosochloride with sodium and methyl alcohol, crystallises in rhomboids, m. p. 116°, is optically inactive, and yields a crystalline *additive* compound with bromine.

β-*Nitrosocaryophyllene*, formed by reduction of the nitrosochlorides, crystallises in needles, m. p. 120—121°, $[\alpha]_D$ +61·77°.

The blue caryophyllene nitrosite, m. p. 115°, $[\alpha]_D$ +102·95°, when treated successively with potassium hydroxide and acetic acid in alcoholic solution, is converted into a unimolecular *isomeride*, which crystallises in colourless needles, m. p. 139—139·5°, $[\alpha]_D^{18}$ +120·0°, forms greenish-blue solutions in glacial acetic acid or alcohol, decolorises bromine in glacial acetic acid solution, and if heated with glacial acetic acid forms a crystalline *substance* resembling nitrocaryophyllene.

If the solution of the blue nitrosite in alcoholic potassium hydroxide is acidified with acetic acid only after four hours, it yields d-*nitrosocaryophyllene*, $C_{15}H_{23}ON$, crystallising in needles, m. p. 162—163°, $[\alpha]_D^{18}$ +209·2°; this substance is unimolecular, and decolorises bromine in glacial acetic acid solution or more slowly in carbon tetrachloride solution.

When the blue nitrosite is boiled with light petroleum in a current of carbon dioxide, the solution becomes green and finally yellow, evolves nitric oxide, and deposits a voluminous precipitate containing (*a*) a *substance*, $C_{15}H_{23}O_6N_4$ or $C_{15}H_{23}O_7N_8$, which crystallises from acetone on addition of light petroleum in silky needles, m. p. 159° (decomp.), and dissolves in aqueous potassium hydroxide, but is optically inactive and does not decolorise bromine, and (*b*) a *nitrosite*, $C_{15}H_{22}O_4N_2$, which crystallises in flat needles, m. p. 130·5°, decolorises bromine in glacial acetic acid solution, and is optically inactive.

The action of boiling alcohol on the blue nitrosite leads to the formation of a *substance* crystallising in needles, m. p. 128°.

A new *sesquiterpene*, $C_{15}H_{24}$, is obtained from the light petroleum mother-liquor from the preparation of blue caryophyllene nitrosite as an oil, b. p. 123—124°/14·5 mm., $[\alpha]_D$ −25·03°, D^{20} 0·8990, n_D^{20} 1·49617, and with nitrosyl chloride forms a *nitrosochloride*, m. p. 122°, together with traces of α-caryophyllene nitrosochloride, derived probably from a small admixture of caryophyllene, and an *oil*, $[\alpha]_D$ −17°, which distils in a current of steam. Whether the new sesquiterpene is formed during the preparation of the nitrosite or is present originally in the caryophyllene remains undecided.

The resemblance of the reactions of α-caryophyllene nitrosochloride to those of caryophyllene alcohol suggests that these substances are closely related in their constitutions. G. Y.

Components of Ethereal Oils. Sesquiterpene Cedrene. FRIEDRICH W. SEMMLER and ALFRED HOFFMANN (*Ber.*, 1907, **40**, 3521—3528. Compare Rousset, Abstr., 1898, i, 595).—Cedrene, b. p. 124—126°/12 mm., D^{15} 0·9354, α_D −55° (100 mm. tube), n_D 1·50233, yields, on oxidation with potassium permanganate, *cedreneglycol*, $C_{15}H_{26}O_2$, which separates from acetone in centimetre-long columnar prisms, m. p. 160°, b. p. 186—187°/11 mm., D^{15} 1·053; it is very resistant towards permanganate and only reacts very slowly with acetic anhydride. Another product of the oxidation is *cedrene-keto-aldehyde* or *diketone*, $C_{15}H_{24}O_2$, b. p. 165°/10 mm., D^{15} 1·055, the *disemicarbazone* of which has m. p. 234°. The chief product is *cedrene-ketonic acid*, $C_{15}H_{24}O_3$, b. p. 215—222°/11 mm.; the *semicarbazone* has m. p. 245°; the *oxime*, m. p. about 60°, whilst the *methyl* ester, b. p. 160—165°/8 mm., D^{15} 1·054, n_D 1·484, forms a *semicarbazone*, m. p. 180°. *Methyl cedrenedicarboxylate* has b. p. 165—173°, n_D 1·47936, D^{15} 1·081.

Cedrone, $C_{15}H_{22}O$, formed by oxidation of cedrene with chromic acid, is a slightly yellow oil with an intense odour of cedarwood, b. p. 147—150°, $D^{12·5}$ 1·011, n_D 1·51202, a_D $-91°30'$ (100 mm. tube), and forms a semicarbazone, m. p. 242—243°. The reduction product, *dihydroisocedrol*, $C_{15}H_{26}O$, shows b. p. 148—151°/9·5 mm., D^{18} 1·007, n_D 1·51202, $[a]_D$ $-20°30'$. In addition to cedrone, another ketone is formed, b. p. 148—152°/10 mm., D^{16} 1·005, a_D $-40°$. Crude cedrone forms an *oxime*, b. p. 160—180°/11 mm., and this gives rise to an *amine*, b. p. 145—150°, D^{15} 0·979, n_D 1·5097, a_D $-20°36'$.

Dihydrocedrene, $C_{15}H_{26}$, has b. p. 116—122°/10 mm., D^{15} 0·9052, n_D 1·48721. E. F. A.

First Runnings from Finnish Turpentine Oil. OSSIAN ASCHAN (*Zeitsch. angew. Chem.*, 1907, **20**, 1811—1816. Compare Atterberg, Abstr., 1880, 663; Harries, Abstr., 1898, i, 232; Aschan, Abstr., 1906, i, 442, 686).—The yellowish-brown colour and characteristic suffocating odour of the turpentine oil obtained by the distillation of the roots of Finnish pines and firs, *Pinus abies* and *P. sylvestris*, is chiefly due to the presence of diacetyl and its homologues, and the quinones derived from these compounds by condensation. In addition to these compounds, the fraction, b. p. 20—160°, obtained from Finnish turpentine oil, was found on investigation to contain simple aldehydes, furan, sylvan, benzene, toluene, *m*-xylene, methyl esters of fatty acids, furfuraldehyde, unsaturated compounds (probably hydrocarbons), and probably 2:5-dimethylfuran. The fraction, b. p. 100—105°, obtained from the fraction, b. p. 20—160°, gave a red coloration with a pine shaving moistened with hydrochloric acid similar to that obtained with pyrrole. However, the fraction contains no nitrogen, so that this reaction cannot be employed as a test for pyrrole in distillation products obtained from wood. W. H. G.

American Colophony. PAUL LEVY (*Ber.*, 1907, **40**, 3658—3660).—The statement made that the abietin obtained by the distillation of abietic chloride (Abstr., 1906, i, 870) is identical with Kraemer and Spilker's substance from colophony (Abstr., 1900, i, 150) has been confirmed by a careful fractionation of the crude oil from the dry distillation of American colophony.

Abietic acid is indifferent to molten alkali and to the usual reducing agents, although it forms with hydrogen bromide an additive product pointing to this acid containing two ethylenic linkings.

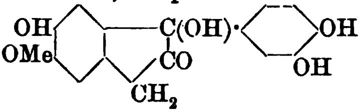
W. R.

Chemical Examination of Eriodictyon Glutinosum. II. GUSTAV MOSSLER (*Monatsh.*, 1907, **28**, 1029—1039. Compare Power and Tutin, Abstr., 1906, ii, 885; Trans., 1907, **91**, 887).—Eriodictyonone has $[a]_D^{20}$ $-28·21°$. It is now found that eriodictyonone tetra-acetate does not form an additive compound with bromine, and, further, that the supposed tetrabromide is a *dibromo*-derivative, $C_{16}H_{12}O_6Br_2$; hence eriodictyonone cannot contain an ethylene linking. The presence of a carbonyl group is confirmed by the formation in alcoholic-acetic acid solution of a *phenylhydrazone*, $C_{16}H_{14}O_5{:}N_2HPh$, which separates in yellow crystals, m. p. 184—186°. Neither eriodictyonone nor its tetra-acetate is oxidised by potassium permanganate in neutral solution; in presence of an alkali, there is obtained the resin formed by the action of alkalis alone.

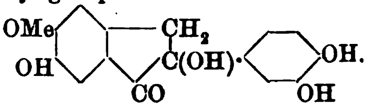
When heated with fuming hydrochloric acid in a sealed tube at 120°, eriodictyonone yields catechol and an *oil*, which gives a green coloration with alcoholic ferric chloride, and is probably an impure *homocatechol*, $C_6H_3Me(OH)_2$.

The action of diazomethane on eriodictyonone leads to the formation of a *methyl ether*, $C_{15}H_{10}O_4(OMe)_2$, which crystallises in prisms, m. p. 160°, reduces ammoniacal silver solution, forms a red resin when heated with aqueous alkalis, and gives a red coloration with alcoholic ferric chloride. On further treatment with an excess of diazomethane, this ether yields the *tetramethyl ether*, $C_{15}H_8O_2(OMe)_4$, which crystallises in yellow needles, m. p. 162°, is insoluble in aqueous alkalis, and does not give a coloration with ferric chloride. When fused with potassium hydroxide, the tetramethyl ether forms protocatechuic acid.

In the light of these results, it is considered that the constitution of eriodictyonone must be represented by the formula I or II. In both cases, the position of the methoxyl group remains undecided.



(I.)



(II.)

(see also Power and Tutin, Proc., 23, 243). G. Y.

Spectrophotometry of the Chlorophyllins and the Energetics of Chlorophyll. M. Tsvett (*Ber. deut. bot. Ges.*, 1907, **25**, 388—397. Compare this vol., i, 787).—Results obtained with an alcoholic solution of chlorophyllin show that the absorption is greater in the blue portion of the spectrum than in the red. The band λ 460—475 can be distinguished in solutions so diluted that the band in the red portion is no longer visible. N. H. J. M.

Phylloxanthin. M. Tsvett (*Biochem. Zeitsch.*, 1907, **6**, 373—378). —A reply to Marchlewski's criticism (this vol., i, 867) of the conclusions drawn by the author (this vol., i, 787). The spectrum of phylloxanthin is very similar to that of β-chlorophyllan; neither substance can be transformed into phyllocyanin. G. B.

New Method of Preparing Azophenin. Wladimir Schaposchnikoff (*Zeitsch. Farb.-Ind.*, 1907, **6**, 289—291).—Details are given for preparing quinonedichlorodi-imine by the action of a solution of bleaching powder on *p*-phenylenediamine or its hydrochloride; by the method used, a pure white product is readily obtained. It is best converted into azophenin by adding aniline to its solution in benzene; other substances are also formed, but azophenin is the principal product (2·8 grams of azophenin from 3·5 grams of quinonedichlorodi-imine), and can be easily separated in a pure state. W. A. D.

Oxidation of Aromatic Amines by Means of Manganese Salt with Formation of Dyes. Fritz Croner (*Chem. Zeit.*, 1907, **31**, 948—949).—If 10 c.c. of a 0·2% aqueous solution of atoxyl [monosodium *p*-aminophenylarsonate] are treated with 10 drops of an 8% manganous chloride solution free from iron and three drops of 20% ammonia, and the resulting precipitate dissolved by addition of a moderate excess of sulphuric acid to the mixture, there is obtained an intense red solution. The red substance is not extracted by shaking with amyl alcohol. The coloration is not produced if the precipitate and reaction liquid are treated with acid separately. Colorations are obtained in the same manner with primary or secondary aromatic amines, but not with tertiary amines, nitroamines, or acylamines. These results confirm Ehrlich and Bertheim's formula for atoxyl (this vol., i, 812). Descriptions are given of the colorations obtained with numerous aromatic amino- and diamino-compounds; where the resulting substance is soluble in amyl alcohol, the colour of the extract is also given.

The amount of dye formed is proportional to the manganese salt and not to the alkali added. The colour reaction takes place in presence of mercuric chloride or arsenious acid, but is diminished in intensity by addition of small amounts of hydrogen cyanide or thiocyanate, and is suppressed completely when these are present in molecular proportion to the manganese salt. Similar colour reactions are obtained in this manner, but only in isolated cases with ferrous chloride; nickel, chromium, and copper salts do not give colorations. G. Y.

Methylfurfur*anti*aldoxime. Correction. WILHELM MEIGEN (*Ber.*, 1907, 40, 3567—3568. Compare this vol., i, 232).—The compound, m. p. 51—52°, previously regarded as a mixture of the *syn-* and *anti*-forms of the oxime, is now shown to be pure methylfurfur*anti*-aldoxime. E. F. A.

Hydroperbromides of Negatively-Substituted 4-Pyrones. FRANZ FEIST (*Ber.*, 1907, 40, 3647—3652. Compare Abstr., 1905, i, 914; 1906, i, 974).—Contrary to Hantzsch and Denstorff's view that only oxides having relatively strong basic properties are capable of forming hydroperbromides, crystalline, more or less stable hydroperbromides have been prepared from 4-pyrones with feeble or no basic properties.

Hydroperbromides of bromo- and dibromo-2 : 6-dimethyl-4-pyrones were shown previously to exist in the crude product of the action of undiluted bromine on 2 : 6-dimethyl-4-pyrone; the composition of this crude product is found now to have undergone little change in two years. The pure hydroperbromides are prepared by the action of bromine and hydrogen bromide on bromo- and dibromo-2 : 6-dimethyl-4-pyrones.

3-*Bromo*-2 : 6-*dimethyl*-4-*pyrone hydroperbromide*, $(C_7H_7O_2Br)_2,HBr,Br_2$, forms a yellow, crystalline powder, decomp. 150°.

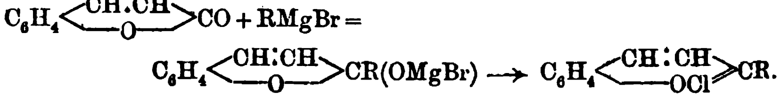
3 : 5-*Dibromo*-2 : 6-*dimethyl*-4-*pyrone hydroperbromide*, $(C_7H_6O_2Br_2)_2,HBr,Br_2$, decomp. 147—148° when freshly prepared, decomposes only slowly at

the ordinary temperature, and can be recrystallised repeatedly from chloroform containing traces of bromine, from which it separates in glistening crystals.

Ethyl chelidonate and ethyl dibromochelidonate form *hydroperbromides*, $C_{11}H_{12}O_6,HBr,Br_7$ and $C_{11}H_{10}OHBr_2,HBr,Br_5$, respectively, which crystallise in reddish-brown needles or prisms, but are less stable than the hydroperbromides of the brominated dimethylpyrones, decomposing when washed with ether or light petroleum or on exposure to air, evolving fumes of bromine and hydrogen bromide. G. Y.

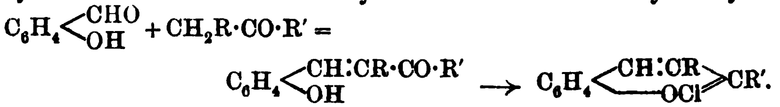
Synthesis of Benzopyrylium Derivatives. Herman Decker and Theodor von Fellenburg (*Ber.*, 1907, 40, 3815—3818).

—Benzopyrylium derivatives may be prepared by the method employed by Bünzly and Decker (Abstr., 1904, i, 912) in the synthesis of xanthonium compounds; thus, 2-substituted benzopyrylium compounds are obtained by the action of magnesium alkyl bromides on coumarin:

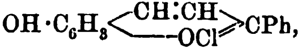


$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH{:}CH}{O}{>}CO + RMgBr =$$
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH{:}CH}{O}{>}CR(OMgBr) \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{CH{:}CH}{OCl}{\geqslant}CR.$$

They also result from the ring-condensation of the products obtained by the interaction of acetaldehyde or ketones and salicylaldehyde:



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CHO}{OH} + CH_2R{\cdot}CO{\cdot}R' =$$
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH{:}CR{\cdot}CO{\cdot}R'}{OH} \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{CH{:}CR}{OCl}{\geqslant}CR'.$$



Hydrogen chloride passed into a mixture of resorcylaldehyde, and acetophenone precipitates 7-*hydroxy*-2-*phenylbenzopyrylium chloride*, $OH{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{CH{:}CH}{OCl}{\geqslant}CPh$, identical with the compound obtained by Bülow and Sicherer (Abstr., 1902, i, 113) from benzoylacetaldehyde and resorcinol. The compounds obtained by Bülow (Abstr., 1901, i, 400, 559; 1902, i, 113) from 1 : 3-diketones and dihydroxybenzenes are therefore hydroxybenzopyrylium salts. The formulæ of these compounds must consequently contain 1 mol. of water less than is present in the formulæ assigned to them by Bülow; this mol. of water is really present as water of crystallisation.

7-Hydroxy-2-phenylbenzopyrylium picrate loses its water of crystallisation at 100° without undergoing decomposition as stated by Bülow and Sicherer (*loc. cit.*). W. H. G.

Synthesis of Leuco-coumaranketones. Stanislaus von Kostanecki, Victor Lampe, and Ch. Marschalk (*Ber.*, 1907, 40, 3660—3669).

—The synthesis of *p*-benzoylcoumarans was attempted in order to throw further light on the constitution of catechin (compare this vol., i, 73). Two methods were tried: (1) the conversion of *p*-hydroxybenzophenone into the corresponding coumaran derivative, (2) interaction of aromatic acid chlorides in the presence of aluminium chloride on coumaran and its substitution derivatives. The first method did not yield the desired result. By the condensation of 3-chloro-4-hydroxybenzophenone and ethylene dibromide in the presence of sodium methoxide, 3-*chloro*-4-*β*-*bromoethoxybenzophenone*,

$$CH_2Br\cdot CH_2\cdot O\cdot C_6H_3Cl\cdot COPh,$$

is formed as chief product. It crystallises in small, white plates, m. p. 79—80°. There is also formed the sparingly soluble 4 : 4″-*ethylenedioxy-bis-3-chlorobenzophenone*, $C_2H_4(O\cdot C_6H_3Cl\cdot COPh)_2$, crystallising in white needles, m. p. 224—226°. All attempts, however, to close the coumaran ring by the Wurtz reaction were unsuccessful, and the same remark applies to the bromo-derivatives. 3-*Bromo*-4-*β*-*bromoethoxybenzophenone*, $C_{15}H_{12}O_2Br_2$, crystallises in white leaflets from dilute alcohol, m. p. 96—97°; the 4 : 4″-*ethylenedioxy-bis*-3 *bromobenzophenone*, $C_{28}H_{20}O_4Br_2$, m. p. 229—230°. 3 : 5-*Dibromo*-4-*β*-*bromoethoxybenzophenone*, $C_{15}H_{11}O_2Br_3$, crystallises in white plates, m. p. 106—107°; the corresponding *ethylenedioxy*-derivative,

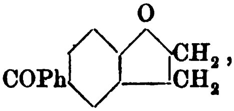
$$C_{28}H_{18}O_4Br_4,$$

has m. p. 217—218°.

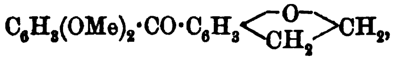
4-*β*-*Bromoethoxybenzophenone*, $C_{15}H_{13}O_2Br$, which crystallises in prisms from alcohol, m. p. 72°, does not yield *p*-benzoylcoumaran on treatment with aluminium chloride; the product obtained is *p*-benzoylphenol. The corresponding *ethylenedioxy*-compound, $C_{28}H_{22}O_4$, has m. p. 195°.

Coumaran itself reacts easily with aromatic acid chlorides in the presence of aluminium chloride and from analogy to the phenol ethers, the conclusion is drawn that substitution occurs in the para-position to the oxygen atom.

4-*Benzoylcoumaran*,

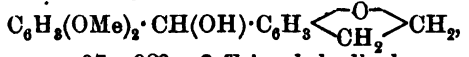


m. p. 44°, crystallises from light petroleum in the triclinic system [$a : b : c = 1·4568 : 1 : 1·8354$; α 101°32′, β 109°45′, γ 103°9′]. By reduction of an alcoholic solution, the *leuco*-p-*benzoylcoumaran* was obtained as a viscous oil; it is conjectured to be the parent substance of catechin. 4-*Veratroylcoumaran*,



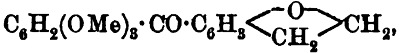
$$C_6H_3(OMe)_2\cdot CO\cdot C_6H_3\left<\begin{matrix}O\\CH_2\end{matrix}\right>CH_2,$$

crystallises in stout, white prisms, m. p. 136—137°, and gives on reduction *leuco*-4-*veratroylcoumaran*,



$$C_6H_3(OMe)_2\cdot CH(OH)\cdot C_6H_3\left<\begin{matrix}O\\CH_2\end{matrix}\right>CH_2,$$

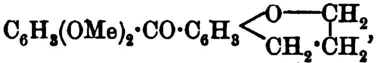
stout prisms, m. p. 97—98°. 2-*Trimethylgalloylcoumaran*,



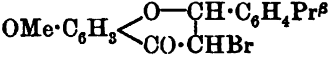
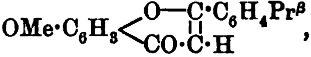
$$C_6H_2(OMe)_3\cdot CO\cdot C_6H_3\left<\begin{matrix}O\\CH_2\end{matrix}\right>CH_2,$$

forms needles, m. p. 110—111°, and its *leuco*-compound, $C_{18}H_{20}O_3$, forms leaflets, m. p. 108—109°.

Chroman also combines with acid chlorides to form similar derivatives. 6-*Benzoylchroman*, $C_{16}H_{14}O_2$, is an oil, b. p. 365°/710 mm., solidifying to a crystalline mass in a cold mixture. 6-*Veratroyl*-

chroman,  $C_6H_3(OMe)_2{\cdot}CO{\cdot}C_6H_3{<}\begin{array}{l}O\text{——}CH_2\\CH_2{\cdot}CH_2\end{array}$, crystallises in white needles, m. p. 103—104°; its *leuco*-compound, $C_{18}H_{20}O_4$, forms prisms, m. p. 115—116°.

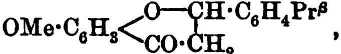
The following compounds are also described: p-*veratroyl*-o-*ethylanisole*, $C_6H_3(OMe)_2{\cdot}CO{\cdot}C_6H_3Et{\cdot}OMe$, which crystallises in white needles, m. p. 103—104°, and its *leuco*-derivative, $C_{18}H_{22}O_4$, white needles, m. p. 84—85°; p-*trimethylgalloyl*-o-*ethylanisole*, $C_{19}H_{22}O_5$, m. p. 105°, the *leuco*-compound has m. p. 86—88°. W. R.

Further Synthesis in the Flavone Group. STANISLAUS VON KOSTANECKI (*Ber.*, 1907, 40, 3669—3677).—[With M. KOLKER.]—6-*Hydroxy*-4′-iso*propylflavone*, $C_{19}H_{20}O_3$, prepared by the interaction of quinacetophenone monomethyl ether, cumenol, and sodium hydroxide, crystallises from alcohol in colourless leaflets, m. p. 90°. 3-*Bromo*-6-*methoxy*-4′-iso*propylflavanone*,  $OMe{\cdot}C_6H_3{<}\begin{array}{l}O\text{—}CH{\cdot}C_6H_4Pr^{\beta}\\CO{\cdot}CHBr\end{array}$, obtained by brominating the corresponding methoxy*iso*propylflavanone in carbon disulphide, forms white needles, m. p. 125—127°. Like all 3-bromoflavanones when treated with concentrated potassium hydroxide in alcoholic solution, hydrogen bromide is eliminated and 6-*methoxy*-4′-iso*propylflavone*,  $OMe{\cdot}C_6H_3{<}\begin{array}{l}O\text{—}C{\cdot}C_6H_4Pr^{\beta}\\CO{\cdot}C{\cdot}H\end{array}$, is obtained; it crystallises from dilute alcohol in white leaflets, m. p. 135°. On heating with hydriodic acid, 6-*hydroxy*-4′-iso*propylflavone*, $C_{18}H_{16}O_3$, is formed, and from alcohol gives pale yellow needles, m. p. 182—183°.

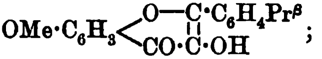
[With A. TOBLER.]—2′-*Hydroxy*-4′-*methoxy*-4-iso*propylchalkone*,

$$OMe{\cdot}C_6H_3(OH){\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4Pr^{\beta},$$

prepared by condensing cumenol with pæonol, crystallises from alcohol in yellow leaflets, m. p. 104°. When an alcoholic solution of this compound is heated with dilute hydrochloric acid for twenty-four hours, it is transformed into 7-*methoxy*-4′-iso*propylflavanone*,



$$OMe{\cdot}C_6H_3{<}\begin{array}{l}O\text{—}CH{\cdot}C_6H_4Pr^{\beta}\\CO{\cdot}CH_2\end{array},$$

which crystallises in prisms, m. p. 75°. Amyl nitrite and hydrochloric acid convert the flavanone into the *iso*nitroso-derivative, which, however, is unstable, and there results 7-*methoxy*-4′-iso*propylflavanol*,  $OMe{\cdot}C_6H_3{<}\begin{array}{l}O\text{—}C{\cdot}C_6H_4Pr^{\beta}\\CO{\cdot}C{\cdot}OH\end{array}$; it crystallises in pale yellow, glistening leaflets, m. p. 201°. Like all flavanols, the yellow *sodium* salt is sparingly soluble; the *acetate*, $C_{21}H_{20}O_5$, has m. p. 163—164°. Reduction of the methoxy*iso*propylflavanol with hydriodic acid gives rise to 7-*hydroxy*-4′-iso*propylflavanol*, $C_{18}H_{16}O_4$, which forms almost colourless leaflets, m. p. 243°; the *diacetate*, $C_{22}H_{20}O_6$, crystallises in white needles, m. p. 124°.

[With H. RABINOWITSCH.]—2′-*Hydroxy*-3′:4′-*dimethoxy*-4-iso*propylchalkone*, $OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4Pr^{\beta}$, prepared from gallacetophenone dimethyl ether and cumenol in the presence of

50% sodium hydroxide, crystallises in yellow leaflets, m. p. 114°, and forms the starting point for the preparation of the 7:8-dihydroxy*iso*propylflavanol in a similar manner to that of the 7-hydroxy-compound.

7:8-*Dimethoxy*-4′-iso*propylflavanone*, $C_{20}H_{22}O_4$, forms small, white, granular crystals, m. p. 92°. The iso*nitroso*-derivative, $C_{20}H_{21}O_5N$, is stable and has m. p. 173°.

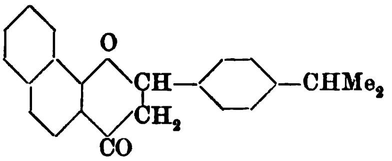
7:8-*Dimethoxy*-4′-iso*propylflavanol*, $C_{20}H_{20}O_5$, forms pale yellow needles, m. p. 162°, and yields an intensely yellow *sodium* salt; the *acetate*, $C_{22}H_{22}O_6$, white needles, m. p. 152°.

7:8-*Dihydroxy*-4′-iso*propylflavanol*, $C_{18}H_{16}O_5$, crystallises in glistening leaflets, m. p. 265°; the *diacetate*, $C_{24}H_{22}O_8$, forms white needles, m. p. 152°.

[With G. Stenzel.]—2-*Cumenylideneaceto*-1-*naphthol*,

$$OH{\cdot}C_{13}H_6{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4Pr^{\beta},$$

prepared from cumenol and 2-aceto-1-naphthol under similar conditions to the benzylidene compound (compare Abstr., 1898, i, 369), crystallises from alcohol in orange-red prisms, m. p. 98°; the *acetate*, $C_{24}H_{22}O_3$, is pale yellow, m. p. 88—89°. 4′-iso*Propyl*-α-*naphthaflavanone* (annexed formula) forms colourless prisms, m. p. 134—135°; the corresponding *flavanol*, $C_{22}H_{18}O_3$, crystallises in pale yellow needles, m. p. 211—212°; the *acetate*, $C_{24}H_{20}O_4$, is white, m. p. 157°. W. R.



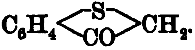
Preparation of Santalyl Esters. Chemische Fabrik von Heyden (Aktien-Gesellschaft) (D.R.-P. 182627. Compare Abstr., 1906, i, 972).—The santalyl esters of the higher fatty acids from valeric acid onwards do not possess the unpleasant odour and irritating properties of free santalol and its esters with acetic acid and its immediate homologues.

Santalyl stearate, a clear yellow oil, is prepared by mixing santalol and stearyl chloride and completing the reaction on the water-bath; it separates on the addition of alcohol.

Santalyl valerate and *santalyl oleate* resemble the preceding compound, and are prepared respectively in a similar manner from valeryl and oleyl chlorides and santalol. G. T. M.

Preparation of Thionaphthen Derivatives. Kalle & Co. (D.R.-P. 184469).—*o*-Aminophenylthioglycollic acid, prepared from *o*-thioaniline and chloroacetic acid, when diazotised and treated with potassium cuprocyanide furnishes *o*-*cyanophenylthioglycollic acid*, yellowish needles, m. p. 142°. This substance on hydrolysis with aqueous sodium hydroxide yields 3-*amino*-(1)-*thionaphthen*-2-*carboxylic acid*, which on further treatment with alkali gives rise to 3-hydroxy-

(1)-thionaphthen-2-carboxylic acid and 3-hydroxy-(1)-thionaphthen,



$C_6H_4\left\langle\begin{matrix}S\\CO\end{matrix}\right\rangle CH_2$.

G. T. M.

Some New Alkaloids from Plants. Amé Pictet and G. Court (*Ber.*, 1907, 40, 3771—3783; *Bull. Soc. chim.*, 1907, [iv], 1, 1001—1016).—The hypothesis put forward by Pictet (Abstr., 1905, i, 541) receives support from the fact that alkaloids of simple structure are obtained by steam distillation from plants which have been treated with dilute sodium carbonate solution.

The concentrated aqueous extract of tobacco leaves ("raw nicotine") yields, when distilled at 80—120°, an alkaline distillate from which pyrrolidine and 1-methylpyrroline were isolated and identified by means of their auri- and platini-chlorides. 1-*Methylpyrroline picrolonate* crystallises in yellow prisms, m. p. 222° (decomp.).

Black pepper yields a distillate which does not contain piperidine as stated by Johnstone (Abstr., 1889, 298), but a *base* which is probably a *C*-methylpyrroline, C_5H_9N; the *aurichloride*, $C_5H_9N,HAuCl_4$, crystallises in yellow leaflets or flat needles, m. p. 182°; the *picrolonate* is a yellow, crystalline powder, m. p. 217°; the *platinichloride*,

$$(C_5H_9N)_2,H_2PtCl_6,$$

m. p. 203°, forms microscopic, orange prisms.

The distillate from carrot leaves was found to contain pyrrolidine and a new base, *daucine*, $C_{11}H_{18}N_2$, a colourless, oily liquid with a nicotine-like odour, b. p. 240—250°, $[\alpha]_D$ +7·74° in ether. The *hydrochloride* forms long needles; no precipitate is produced on adding auric, platinic, or mercuric chloride to a solution of the hydrochloride. The hydrochloride when heated with zinc dust does not give a coloration with a pine shaving. The *base* obtained from carrot seeds is not identical with daucine, since it gives the pyrrole reaction and its *aurichloride*, m. p. 172—175° (decomp.), is insoluble.

The leaves of parsley yield a *base*, the crystalline *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust; no precipitate is obtained on adding auric or platinic chloride to a solution of the hydrochloride; the *picrolonate* forms yellow, microscopic needles, m. p. 210°.

Coca leaves yield a *base*, the *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust. No precipitate is formed on adding picric acid, auric or platinic chloride to a solution of the hydrochloride; picrolonic acid produces a yellow, flocculent precipitate.

The authors consider that, since the above bases, with the exception of daucine, belong to the pyrrole group, they are probably derived from the plant albumin.

W. H. G.

Cinchona Alkaloids. VII. A New Oxidation Product of Cinchonine. Paul Rabe [with Ernst Ackermann and W. Schneider] (*Ber.*, 1907, 40, 3655—3658).—An intermediate product of the oxidation of cinchonine by chromic acid in either sulphuric acid or glacial acetic acid has been isolated in small quantity. It is a *base*,

$C_{19}H_{20}ON_2$, containing two atoms of hydrogen less than cinchonine, and crystallises in pale yellow needles, m. p. 126—127°, $[\alpha]_D^{20}$ $+68·8°$ in 3·3% alcoholic solution. Although a strong base, it also dissolves in aqueous alkali hydroxides, from which it is precipitated by carbon dioxide. It is oxidised by chromic acid to cinchonic acid and meroquinenine; potassium permanganate and bromine are, however, without action. The *hydrochloride*, $C_{19}H_{20}ON_2,HCl$, crystallises in white needles, m. p. 245—247°; the *methiodide*, has m. p. 232—233°, and the *dihydroiodide* is oily. The base combines with hydroxylamine.

W. R.

True and False (Pseudo-) Commercial Tannates of Quinine.

PIETRO BIGINELLI (*Gazzetta*, 1907, **37**, ii, 205—226).—Tannic acid is capable of forming, with the ordinary salts of quinine, additive compounds which are usually yellow. Such compounds, containing variable proportions of tannic acid, are always obtained when solutions of tannic acid act on quinine salts. Many of the commercial quinine tannates are compounds of this nature, retaining some of the qualities of the quinine salts from which they have been prepared, and are hence termed pseudo- or false tannates. Quinine pseudo-tannates of constant composition can be prepared under constant conditions. The percentage of quinine in these compounds varies from 18 to 39. Tannic acid is not capable of displacing sulphuric or hydrochloric acid from its combination with quinine. True quinine tannates can only be prepared by mixing solutions of the base and acid in proportions varying according to the tannate required.

The following compounds have been prepared and analysed.
(1) True quinine tannates: $C_{20}H_{24}O_2N_2,C_{14}H_{10}O_9,3H_2O$;
$C_{20}H_{24}O_2N_2,2C_{14}H_{10}O_9,6H_2O$; $C_{20}H_{24}O_2N_2,3C_{14}H_{10}O_9,10H_2O$.
(2) False or pseudo-tannates: $4(C_{20}H_{24}O_2N_2,H_2SO_4),5C_{14}H_{10}O_9,13H_2O$;
$2(C_{20}H_{24}O_2N_2,H_2SO_4),5C_{14}H_{10}O_9,20H_2O$;
$2(C_{20}H_{24}O_2N_2H_2SO_4),7C_{14}H_{10}O_9,25H_2O$;
$2C_{20}H_{24}O_2N_2,H_2SO_4,5C_{14}H_{10}O_9,20H_2O$;
$2(C_{20}H_{24}O_2N_2,2HCl),5C_{14}H_{10}O_9,13H_2O$;
$C_{20}H_{24}O_2N_2,2HCl,5C_{14}H_{10}O_9,xH_2O$.

T. H. P.

A Base Obtained in the Working Up of the Alkaloids Occurring with Cocaine.

CARL LIEBERMANN (*Ber.*, 1907, **40**, 3602—3603).—Anhydroecgonine ethyl ester (Einhorn, Abstr., 1887, 741; Willstätter, Abstr., 1901, i, 649) has been found in the ecgonine residues obtained in the separation of the subsidiary alkaloids of crude cocaine. It is formed probably by esterification of anhydroecgonine during the process of separation. The ethyl ester, b. p. 130—132°/11 mm., $[\alpha]_D$ $-51°33'$, is hydrolysed by boiling hydrochloric acid, D 1·125, forming anhydroecgonine. The *picrate*, $C_{11}H_{17}O_2N,C_6H_3O_7N_3$, crystallises in yellow leaflets, m. p. 168°; the platinichloride, m. p. 217° (211°: Einhorn, *loc. cit.*); the *aurichloride*, $C_{11}H_{17}O_2N,HAuCl_4$, forms lemon-yellow granules, m. p. 124°.

G. Y.

***iso*Coniine.** ALBERT LADENBURG (*Ber.*, 1907, **40**, 3734—3736. Compare Abstr., 1906, i, 692).—In consequence of Löffler's suggestion that the high rotatory power of synthetic coniine is due to the presence of allylpiperidine, the author has attempted to prepare the alkaloid by a method which excludes the formation of the unsaturated base. Methylpicolylalkine is reduced by hydriodic acid and amorphous phosphorus at 125°, the product treated with zinc dust and cold water, and the resulting propylpyridine reduced by sodium and alcohol to propylpiperidine, which is resolved by tartaric acid. The liberated base is pure *iso*coniine, and has $[\alpha]_D^{18\cdot5} +17\cdot85°$. C. S.

Morphine. XIV. allo-ψ-Codeine, a New Isomeride of Codeine. LUDWIG KNORR, HEINRICH HÖRLEIN, and CLEMENS GRIMME (*Ber.*, 1907, **40**, 3844—3851).—It has been lately pointed out by Knorr and Hörlein (this vol., i, 789) that, of the two compounds, ψ-codeine and *iso*codeine, quoted in the literature as being isomeric with codeine, ψ-codeine is a structural isomeride of codeine. Uncertainty exists, however, regarding Schryver and Lees' "*iso*codeine" (Trans., 1901, **79**, 576), which is a mixture containing appreciable amounts of ψ-codeine, the presence of the latter doubtless accounting for the ψ-codeinone obtained by the oxidation of "*iso*codeine." In attempting to prepare pure *iso*codeine, the authors have obtained a new base, isomeric with codeine; crude *iso*codeine appears to contain *iso*codeine, ψ-codeine, and small amounts of this new base, which, for the present, is termed *allo-ψ*-codeine. When this new base is oxidised with chromic acid in sulphuric acid solution, it forms ψ-codeinone, and accordingly contains the alcoholic hydroxyl group in position 8.

The melting points and specific rotations of the isomeric morphines, codeines, and methylmorphimethines are quoted in tabular form, and also the melting points and specific rotations of the corresponding methiodides.

From the products of the hydrolysis of chloromorphide, γ-*isomorphine*, a new isomeride of morphine, has been isolated. This compound has m. p. 278°, $[\alpha]_D^{15°} -94°$ (solvent not stated), and its methiodide has m. p. 295° and $[\alpha]_D^{15°} -51°$; when methylated, it forms ψ-codeine [compare, however, Lees (Trans., 1907, **91**, 1408), who has also lately studied the hydrolysis of chloromorphide and obtained, as one of the products, neo*iso*morphine, which seems to be identical with the above-mentioned γ-*iso*morphine].

allo-ψ-Codeine is possibly identical with Lees' β-*iso*codeine. It is prepared as follows from the mixture of bases obtained by the method of Schryver and Lees by the hydrolysis of bromocodeide. Potassium iodide is added to the solution of this crude *iso*codeine in dilute acetic acid, when a mixture of ψ-codeine and *allo-ψ*-codeine hydriodides gradually separates and may be separated by means of absolute alcohol. As an alternative method, crude *iso*codeine is acetylated by means of boiling acetic anhydride and the mixture of acetyl derivatives separated by means of absolute alcohol, in which acetyl *allo-ψ*-codeine is soluble with difficulty, and separates in tiny needles, m. p. 194—195°.

allo-ψ-*Codeine*, obtained either from the hydriodide or the acetyl derivative, is an oil with a bluish-violet fluorescence; it has not yet been obtained crystalline. In absolute alcohol, it has $[\alpha]_D^{15}$ −228° ($c = 4{\cdot}5$). Its *hydriodide* separates from water in spear-shaped crystals decomposing at 280—285°; in aqueous solution, it has $[\alpha]_D^{15}$ −153° ($c = 1{\cdot}967$). It differs from ψ-codeine hydriodide, which crystallises from water in glistening leaflets, contains $1H_2O$, has m. p. 260—265° (decomp.), and $[\alpha]_D^{15}$ −57°.

When *allo*-ψ-codeine is oxidised, it forms ψ-codeinone.

*Acetyl*allo-ψ-*codeine* crystallises from absolute alcohol in needles, m. p. 194—195°, and differs from acetyl-ψ-codeine, which is an oil, and from acetylcodeine, which has m. p. 133·5°. Its *methiodide*, $C_{20}H_{23}O_4N,MeI,EtOH$, separates from absolute alcohol in leaflets, m. p. about 260° (decomp.).

allo-ψ-*Codeine methiodide*, $C_{18}H_{21}O_3N,MeI$, crystallises from methyl alcohol in rectangular leaflets, m. p. about 215° (decomp.). In aqueous solution, it has $[\alpha]_D^{15}$ −142° ($c = 1{\cdot}728$). When boiled with sodium hydroxide, it forms a methine base which, for the present, is termed *ζ-methylmorphimethine*; it is apparently related to ε-methylmorphimethine in the same manner as *allo*-ψ-codeine is related to ψ-codeine. The new base has $[\alpha]_D^{15}$ −174° ($c = 8{\cdot}91$) in alcoholic solution (after treatment with alcoholic potassium hydroxide); when dried until constant in weight, it gave $[\alpha]_D^{15}$ −178° ($c = 10{\cdot}955$) in alcoholic solution. Its *methiodide*, $C_{19}H_{23}O_3N,MeI$, is a colourless powder, m. p. about 180° (indefinite); in aqueous solution, it has $[\alpha]_D^{15}$ −148° ($c = 2{\cdot}486$).

A. McK.

Morphine. XV. Dioxycodeine and Deoxydihydrocodeine.

Ludwig Knorr and Rudolf Waentig (*Ber.*, 1907, **40**, 3860—3868).—In continuation of the work of Knorr and Hörlein (this vol., i, 235), it is found that deoxycodeine is best prepared by the reduction of bromocodeide or chlorocodeide with zinc dust and alcohol in the absence of acid. The reduction product, obtained by means of sodium and alcohol, is, however, not identical, as was formerly supposed, with the product obtained by the action of zinc and hydrochloric acid or of zinc dust and alcohol; it is lævorotatory, whereas the other products are dextrorotatory.

From the dextrorotatory deoxycodeine of Knorr and Hörlein, the lævorotatory base, deoxydihydrocodeine, is obtained by the action of sodium and alcohol.

Deoxycodeine melts at about 126° and crystallises from dilute methyl alcohol in glistening, hexagonal or rhombic leaflets. In alcoholic solution, it has $[\alpha]_D^{15}$ +119—121° ($c = 4{\cdot}9215$).

Deoxycodeine hydrochloride, $C_{18}H_{21}O_2N,HCl,EtOH$, crystallises from absolute alcohol in glistening prisms, which soften at about 165°, and have m. p. about 270° (decomp.); in aqueous solution, it has $[\alpha]_D^{15}$ +84—87°. The *hydriodide*, $C_{18}H_{21}O_2N,HI$, separates from water in needles, m. p. about 265° (decomp.). The *benzoate* crystallises from water in tiny, prismatic needles, m. p. about 188°; in absolute alcohol, it has $[\alpha]_D^{15}$ +106° ($c = 5{\cdot}53$). The *acetyl* derivative is an oil, and forms an *hydriodide*, $C_{20}H_{23}O_3N,HI$, which separates from water in silky needles, m. p. 230° (indefinite), and a *methiodide*,

$$C_{20}H_{23}O_3N,MeI,EtOH,$$

which crystallises from absolute alcohol in yellow needles, m. p. about 270°.

Deoxycodeine forms a glassy methiodide, from the aqueous solution of which a brown oil separates on boiling with sodium hydroxide; when this oil is crystallised from absolute alcohol, it forms yellow prisms, m. p. 162—164°, and is the methine base of deoxycodeine. It is readily oxidised even at the ordinary temperature by the air; its *nitrate*, $C_{19}H_{23}O_2N,HNO_3$, is, however, more stable and separates from acetic acid in silky needles, m. p. 202°.

Methyldeoxycodeine methiodide, $C_{19}H_{23}O_2N,MeI$, obtained by the methylation of deoxycodeine in alkaline solution with methyl sulphate and interaction of the product with potassium iodide, crystallises in glistening leaflets, m. p. 251—252°, with preliminary softening. It has $[\alpha]_D^{15}$ $+108°$ $(c = 2{\cdot}290)$ in alcoholic solution.

When the aqueous solution of methyldeoxycodeine methiodide is boiled with sodium hydroxide, an oil separates, which is very unstable; it decomposes in hydrochloric acid solution giving dimethylmorphol.

Deoxydihydrocodeine, $C_{18}H_{23}O_2N,\frac{1}{2}H_2O$, crystallises from dilute methyl alcohol in glistening leaflets, m. p. about 132°; the anhydrous compound has $[\alpha]_D^{15}$ $-24°$ $(c = 5{\cdot}171)$ in absolute alcoholic solution. Its *hydrochloride*, $C_{18}H_{23}O_2N,HCl,EtOH$, has m. p. about 155° (decomp.), and $[\alpha]_D^{15}$ $-17°$ $(c = 5{\cdot}289)$ in aqueous solution. The *benzoate* separates from ethyl acetate in tetrahedra, m. p. about 180°, and has $[\alpha]_D^{15}$ $-9°$ $(c = 5{\cdot}145)$.

Methyldeoxydihydrocodeine methiodide, $C_{19}H_{25}O_2N,MeI$, obtained by methylating deoxydihydrocodeine with methyl sulphate and then causing the product to react with potassium iodide, separates from water in leaflets and from alcohol in needles, m. p. 248—249° (indefinite), and has $[\alpha]_D^{15}$ $-12°$ $(c = 2{\cdot}773)$ in 99% alcoholic solution.

A. McK.

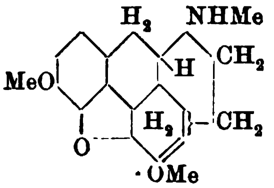
Preparation of Narceine and Homonarceine Derivatives. KNOLL & Co. (D.R.-P. 183589. Compare this vol., i, 236).—Narceine and homonarceine were formerly alkylated by treatment with alkyl sulphates, and it is now found that the same derivatives are obtained by the action of alkyl iodides, methyl phosphate, and methyl nitrate.

Ethylnarceine hydrochloride, m. p. 231°, may be obtained from the product of the interaction of ethyl bromide on the potassium derivative of narceine.

Methylnarceine hydrochloride, m. p. 243°, is produced by treating the potassium derivative of narceine with methyl phosphate and combining the resulting base with hydrochloric acid.

G. T. M.

The Action of Ozone on Thebaine. ROBERT PSCHORR and HANS EINBECK (*Ber.*, 1907, 40, 3652—3654).—Morphine bases are converted into phenanthrene derivatives by treatment with ozone, the side-ring containing nitrogen undergoing rupture. Thebaine, however, behaves differently, the nitrogen ring remains intact, a 60% yield of *a-thebaizone*, $C_{19}H_{21}O_5N$, leaflets, m. p. 125—126° (corr.), is obtained containing two atoms of oxygen more than thebaine. This new compound contains two methoxyl groups like thebaine, and the presence of a carbonyl group is shown by the formation of a *monosemicarbazone*, $C_{20}H_{24}O_5N_4$, which crystallises in flat rods, m. p. 202° (corr.). On dissolution of the thebaizone in dilute sodium hydroxide solution, hydrolysis of one methoxyl group occurs, and the conclusion is drawn that one of the methoxy-groups exists as the ester. The fifth oxygen atom is indifferent. These results, taken in conjunction with those already known about thebaine, lead to the constitution annexed, the grouping $\cdot C(OMe){:}C{:}$ being converted into that represented by $\cdot CO_2Me\cdot C{:}O$. W. R.



A New Base form the Solanaceæ. RICHARD WILLSTÄTTER and WOLFGANG HEUBNER (*Ber.*, 1907, **40**, 3869—3875).—The new *alkaloid*, $C_8H_{20}N_2$, obtained from *Hyoscyamus muticus* in addition to hyoscyamine and other products, is a colourless liquid, b. p. 169° (corr.), and with D^{15} 0·7941; it is miscible with water in all proportions, has a strongly alkaline reaction, and is easily volatile with steam. It exhibits the behaviour of a saturated, ditertiary base. It is quite stable towards permanganate in cold sulphuric acid solution, and does not react with benzenesulphonic chloride and alkali. In moderate doses, it has no poisonous action. The *hydrochloride*, $C_8H_{20}N_2,2HCl$, crystallises in triangular prisms, m. p. 273° (decomp.), is deliquescent, and very readily soluble in water. Its *platinichloride*,

$$C_8H_{20}N_2,H_6PtCl_6,$$

has m. p. 234° (decomp.); its *aurichloride* decomposes at 206—207°.

The *compound*, $C_4H_8(NMe_3I)_2$, forms hygroscopic leaflets or tiny needles, m. p. 305—308° (decomp.). By the distillation of the ammonium base, obtained from the iodide by means of silver oxide, an aqueous distillate was obtained and a gas, which was identified as butadiene by means of the sparingly soluble α-bromide, m. p. 117°, and the more easily soluble bromide, m. p. 39°. The aqueous distillate contained, in addition to trimethylamine, tetramethyldiaminobutane, which was identified by means of its aurichloride.

The preparation of 1 : 4-diaminobutane from succinaldoxime is described, the method used being a modification of the method of Ciamician and Zanetti. The methylation of 1 : 4-diaminobutane is described, hexamethyltetramethylenediammonium chloride being obtained. When the latter compound is distilled, the main product is the monoamine, 1-methylpyrrolidine. 1-Methylpyrrolidine methiodide, $C_6H_{14}NI$, crystallises in prisms, which decompose above 300°; the *aurichloride*, $C_6H_{14}NCl_4Au$, crystallises in hexagonal prisms with pyramidal ends, m. p. 286° (decomp.).

The product of the methylation of tetramethylenediamine, in the form of its chloride, aurichloride, platinichloride, and picrate, was compared with the quaternary derivatives of the solanaceous base investigated, the agreement being complete. The following constitution has accordingly been assigned to the alkaloid:

$$NMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_2.$$

Hexamethyltetramethylenediammonium chloride, $C_4H_8(NMe_3)_2Cl_2$, crystallises from alcohol in prisms; its *picrate* has m. p. 285° (decomp.); its *platinichloride* has m. p. 279° (decomp.); its *aurichloride* decomposes at 304—309°. A. McK.

Rupture of Cyclic Bases by Cyanogen Bromide. JULIUS VON BRAUN (*Ber.*, 1907, **40**, 3914—3933).—The action of cyanogen bromide on cyclic bases either breaks the ring (Abstr., 1900, i, 430) or replaces the alkyl or aryl group attached to the nitrogen atom by the cyanogen group (Abstr., 1902, i, 365). A third alternative is represented by the scheme X N·R + Br·CN = Br·X·NR·CN. The improved methods for the preparation of αδ-dibromobutane and αε-dibromopentane (Abstr., 1904, i, 841) have enabled the author to prepare numerous derivatives of pyrrolidine and piperidine, by means of which he has shown that the rupture of a cyclic base is more easily accomplished by cyanogen bromide than by any other method, a brominated cyanamide being formed in accordance with the preceding scheme.

The reaction between 1-phenylpiperidine and cyanogen bromide leads, after several hours, to the formation of *phenyl-ω-bromoamylcyanamide*, $CH_2Br\cdot[CH_2]_4\cdot NPh\cdot CN$, and the quaternary *bromide*, $C_5NH_{10}PhBr\cdot[CH_2]_5\cdot NPh\cdot CN$. The latter is a brown oil which is identified by conversion into the *platinichloride*, $(C_{23}H_{30}N_3)_2PtCl_6$, m. p. 121—122°. The former is an oil which is soluble in concentrated acids, and by prolonged boiling with 48% hydrobromic acid is converted into the oily *ω-bromoamylaniline hydrobromide*, from an aqueous solution of which the *picrate* is obtained as a yellowish-green powder which sinters at 137° and has m. p. 141°. The *base* is a faintly-coloured, feebly-smelling oil, which yields the *platinichloride*,

$$2CH_2Br\cdot[CH_2]_4\cdot NHPh,H_2PtCl_6,$$

m. p. 117—118°, in reddish-yellow crystals, and by warming changes quantitatively to 1-*phenylpiperidine hydrobromide*, m. p. 235°. 1-*Phenylpiperidine picrate* has m. p. 148°.

Piperidine in excess and phenyl-ω-bromoamylcyanamide react to form *ω-piperidinoamylphenylcyanamide*, $C_5NH_{10}\cdot CH_2\cdot[CH_2]_4\cdot NPh\cdot CN$, b. p. 230—232°/9 mm., of which the *picrate*, m. p. 112°, forms yellow leaflets, and the *methiodide*, m. p. 101°, white leaflets.

Phenylmethylpiperidinium iodide has m. p. 146°; distillation of the hydroxide does not cause a rupture of the ring, but regenerates 1-phenylpiperidine.

1-*p*-Tolylpiperidine, prepared from *p*-toluidine and αε-dibromopentane, has b. p. 268—269° (compare Lellmann and Just, Abstr., 1891, 1244; Scholtz and Wassermann, this vol., i, 339), and behaves with cyanogen bromide in a similar manner to 1-phenylpiperidine. The *bromide*, $C_7H_7\cdot C_5NH_{10}Br\cdot[CH_2]_5\cdot N(C_7N_7)\cdot CN$, m. p. 124—125°, forms hygroscopic, white leaflets. p-*Tolyl-ω-bromoamylcyanamide*, $CH_2Br\cdot[CH_2]_4\cdot N(C_7H_7)\cdot CN$, is an oil which reacts with an excess of *p*-toluidine to form *ω*-p-*toluidinoamyl*-p-*tolylcyanamide*,

$$C_7H_7\cdot NH\cdot CH_2\cdot[CH_2]_4\cdot N(C_7H_7)\cdot CN,$$

m. p. 87°, the *hydrochloride* and *hydrobromide* of which have m. p. 153—154° and 149° respectively. The preceding cyanamide is hydrolysed by 30% sulphuric acid, yielding s-*di*-p-*tolylpentamethylenediamine*, $C_8H_6(CH_2\cdot NH\cdot C_7H_7)_2$, m. p. 60°, of which the *hydrochloride, platinichloride, hydrobromide*, and *sulphate* are mentioned; the *dinitroso*-derivative is a yellow, crystalline powder, m. p. 70—71°, which yields a bishydrazine derivative by reduction. *Dicyanodi*-p-*tolylpentamethylenediamine*, $C_3H_6[CH_2\cdot N(CN)\cdot C_7H_7]_2$, prepared from the diamine and cyanogen bromide in ethereal solution, has m. p. 92°.

1-*p*-Bromophenylpiperidine reacts somewhat slowly with cyanogen bromide, and yields p-*bromophenyl-ω-bromoamylcyanamide*,

$$CH_2Br\cdot[CH_2]_4\cdot N(CN)\cdot C_6H_4Br,$$

m. p. 53°, which by boiling with sodium phenoxide in alcoholic solution forms the *ether*, $OPh\cdot CH_2\cdot[CH_2]_4\cdot N(CN)\cdot C_6H_4Br$, m. p. 60°, b. p. 270—280/10 mm.

1-*iso*Amylpiperidine and cyanogen bromide yield iso*amylpiperidine hydrobromide*, m. p. 255°, and *ω-bromoamyl*iso*amylcyanamide*,

$$CH_2Br\cdot[CH_2]_4\cdot N(CN)\cdot C_5H_{11},$$

which reacts with piperidine to form *ω-piperidinoamyl*iso*amylcyanamide*, $C_5NH_{10}\cdot CH_2\cdot[CH_2]_4\cdot N(CN)\cdot C_5H_{11}$, b. p. 213—215°/12 mm., of which the picrate, platinichloride, aurichloride, methiodide, and methochloride are oils: the *platinichloride* of the last-mentioned, however, forming red crystals, m. p. 145°, sintering at 137°. The preceding cyanamide is hydrolysed by heating with concentrated hydrochloric acid at 130° for fifteen to twenty hours, and yields *ω-piperidinoamyl*iso*amylamine*, $C_5NH_{10}\cdot CH_2\cdot[CH_2]_4\cdot NH\cdot C_5H_{11}$, b. p. 170—172°/9 mm., of which the *picrate* has m. p. 152°.

1-*Butylpiperidine*, $C_5NH_{10}\cdot C_4H_9$, b. p. 175—176°, is obtained from butylamine and *αε*-dibromopentane in 85—90% yield; the *picrate* has m. p. 132°. *Butyl-ω-bromoamylcyanamide*, $CH_2Br\cdot[CH_2]_4\cdot N(CN)\cdot C_4H_9$, reacts with piperidine to form the *compound*

$$C_5NH_{10}\cdot CH_2\cdot[CH_2]_4\cdot N(CN)\cdot C_4H_9,$$

b. p. 206—207/12 mm. C. S.

Compounds of Dichromates of Bivalent Metals with Organic Bases. Nicola Parravano and A. Pasta (*Gazzetta*, 1907, 37, ii, 252—264).—The normal dichromates of bivalent metals, when obtainable, are unstable, but they yield with organic bases well-defined additive compounds which are stable and can be prepared relatively easily.

The compounds prepared by the authors were obtained by adding the organic base to a solution containing potassium dichromate (1 mol.) and the metallic sulphate (1 mol.), or in the case of cadmium, the nitrate.

The *copper dichromate pyridine* compound, $CuCr_2O_7,4C_5NH_5$, forms a green, pulverulent precipitate and dissolves readily in ammonia, giving an intensely green liquid from which can be isolated: (1) the *compound*, $CuCr_2O_7,4NH_3,2H_2O$, in shining, black, prismatic crystals, and (2) the *compound*, $CuCrO_4,4NH_3$, in small, green prisms; both these compounds are decomposed by water. The *copper dichromate aniline* derivative, $CuCr_2O_7,4NH_2Ph$, forms a tobacco-coloured powder decomposable by water. The *copper dichromate ethylenediamine* compound,

$$CuCr_2O_7,2C_2H_4(NH_2)_2,$$

crystallises from water in chestnut-red laminæ.

The *nickel dichromate pyridine* compound, $NiCr_2O_7,4C_5NH_5$, forms pale chestnut prisms; the *aniline* compound, $NiCr_2O_7,4NH_2Ph$, a bright red, crystalline crust decomposable by water; the *ethylenediamine* compounds, $NiCr_2O_7,2C_2H_4(NH_2)_2$, almost black crystals, and

$$NiCr_2O_7,3C_2H_4(NH_2)_2,$$

pale red crystals. The *nickel chromate ethylenediamine* compound,

$$NiCrO_4,3C_2H_4(NH_2)_2,$$

is extremely stable and forms small, dirty yellow prisms.

Cobalt dichromate forms the *compounds*: $CoCr_2O_7,4C_5H_5N$, minute, black crystals; $CoCr_2O_7,4NH_2Ph$, minute, brick-red crystals decomposable by water. The *compound*, $CoCrO_4,2C_2H_4(NH_2)_2$, forms silky, golden-yellow needles.

Cadmium dichromate gives: $CdCr_2O_7,4C_5NH_5$, forming an orange-yellow, crystalline precipitate; $CdCr_2O_7,4NH_2Ph$, as minute, yellow crystals decomposed by water; $CdCr_2O_7,3C_2H_4(NH_2)_2$, as minute, orange-yellow crystals.

Zinc dichromate forms: $ZnCr_2O_7,4C_5NH_5$, which resembles the corresponding cadmium compound, but is not altered by light; $ZnCr_2O_7,3NH_2Ph,H_2O$, which resembles the analogous cadmium derivative in appearance and properties.

Manganese dichromate yields: $MnCr_2O_7,4C_5NH_5$ and

$$MnCr_2O_7,4NH_2Ph,$$

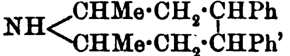
both forming dark chestnut crystals.

All these compounds are in accord with Werner's theory of co-ordination (*Zeitsch. anorg. Chem.*, 1893, **3**, 267; Abstr., 1893, ii, 379).

The solubility of the pyridine derivatives of the dichromates increases, whilst the stability decreases, continuously in the series: copper, nickel, cobalt, cadmium, zinc, manganese. The conductivity of these compounds increases in the order: nickel, cobalt, cadmium, zinc.

T. H. P.

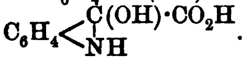
Diphenyldimethylhexamethyleneimine. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 344—349. Compare Harries and de Osa, Abstr., 1903, i, 815).—Reduction of benzylideneacetoxime with aluminium amalgam yields: (1) γ-amino-α-phenylbutane (Harries and de Osa, *loc. cit.*); (2) a *substance*, b. p. much above 238°, and (3) 4:5-*diphenyl*-2:7-*dimethylhexamethyleneimine*,



$NH<\begin{matrix}CHMe\cdot CH_2\cdot CHPh\\ \vert \\ CHMe\cdot CH_2\cdot CHPh\end{matrix}$, which is a colourless, mobile liquid, b. p. 235—238°, with an odour recalling that of piperidine and forming strongly alkaline solutions. Its *benzoyl* derivative, $C_{20}H_{24}NBz$, crystallises from aqueous alcohol in white needles, m. p. 101—102°, and has the normal molecular weight in freezing benzene. The *picrate*, $C_{20}H_{25}N,C_6H_3O_7N_3$, crystallises from benzene or water in yellow needles, m. p. 143—144°; the *oxalate* crystallises from alcohol in nacreous scales, or from aqueous alcohol in slender needles, m. p.

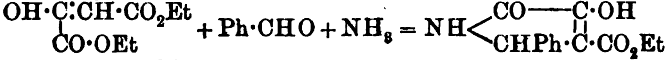
212—213°; the *hydrochloride*, $C_{20}H_{25}N,HCl$, forms white needles, m. p. 154—155°; the *platinichloride*, $(C_{20}H_{25}N)_2,H_2PtCl_6$, crystallises from water in microscopic, pale yellow, rhombic plates, m. p. 185—187°, and the *aurichloride*, $C_{20}H_{25}N,HAuCl_4$, crystallises from water in shining, yellow needles, m. p. 162—163°, and dissolves readily in alcohol.

T. H. P.

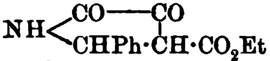
[Preparation of Isatin.] Kalle & Co. (D.R.-P. 184693, 184694).—*o*-Nitromandelic acid, when reduced with zinc dust in an alkaline or ammoniacal solution containing ammonium chloride and the filtered solution treated with excess of concentrated hydrochloric acid, furnishes a yellow, crystalline product, m. p. 162°, which is probably an *anhydride* of o-*hydroxylaminomandelic acid*, $OH\cdot NH\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$, and may be represented by the formula  $C_6H_4<\begin{matrix}C(OH)\cdot CO_2H\\ |\\ NH\end{matrix}$. When this anhydride is melted either alone or preferably with a dehydrating agent, such as acetic anhydride, it gives rise to isatin or acetylisatin respectively. Isatin is also produced when the anhydride is dissolved in aqueous sodium carbonate or hydroxide and the solution subsequently acidified.

G. T. M.

Action of Ethyl Oxalacetate on Aldehydes in Presence of Ammonia and Primary Amines: a New General Reaction of Aldehydes. Louis J. Simon and A. Conduché (*Ann. Chim. Phys.*, [viii], 12, 5—58).—Ethyl oxalacetate readily condenses with aldehydes in presence of ammonia, forming derivatives of 2 : 3-diketopyrrolidine; thus, in the case of benzaldehyde, ethyl 2 : 3-diketo-5-phenylpyrrolidine-4-carboxylate is obtained according to the equation:

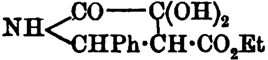
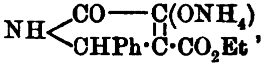


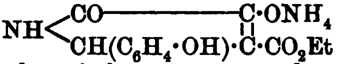
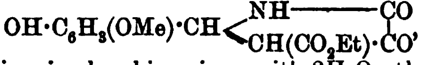
$$\begin{matrix}OH\cdot C{:}CH\cdot CO_2Et\\ |\\ CO\cdot OEt\end{matrix} + Ph\cdot CHO + NH_3 = NH<\begin{matrix}CO\text{——}C\cdot OH\\ \|\\ CHPh\cdot C\cdot CO_2Et\end{matrix} \quad (I) \text{ or}$$

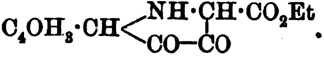
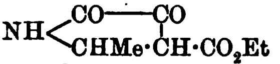


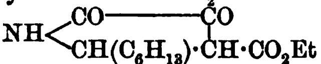
$$NH<\begin{matrix}CO\text{——}CO\\ |\\ CHPh\cdot CH\cdot CO_2Et\end{matrix} \quad (II).$$

If a primary amine is used in place of ammonia, a compound containing the group NR instead of the NH of the pyrrolidine nucleus is obtained. Some of the substances obtained in this way have been described already (Abstr., 1904, i, 521 and 812; 1905, i, 887 and 888; this vol., i, 725). The following facts are new.

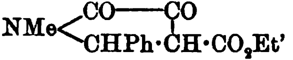
The diketopyrrolidine derivatives, as liberated from their ammonium salts by adding acid, contain $1H_2O$; as this water is not present in the ammonium salts which are derived from the enolic formula (I) above, it is probably combined with the carbonyl group in position 3 in formula II, thus:  $NH<\begin{matrix}CO\text{——}C(OH)_2\\ |\\ CHPh\cdot CH\cdot CO_2Et\end{matrix}$ (III). This water can be expelled by heating in a vacuum at 100°; the anhydrous substance remaining sometimes takes up water again from the atmosphere (salicylic and piperonylic derivatives), but in other cases does not do so. The substance decomposing at 185°, obtained from benzaldehyde and previously given the formula I above (Abstr., 1904, i, 522), is really the hydrated substance (III); when dehydrated, it decomposes at the same temperature, 185°. The *ammonium* salt,  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CO{-}{-}C(ONH_4)}\\ \mathrm{CHPh\cdot C\cdot CO_2Et}\end{array}$, decomposes at 175°; the analogous *aniline* salt melts at 160°, and the p-*toluidine* salt decomposes at 173°; the last two substances, when heated at 120—130°, lose the whole of the combined base, leaving the anhydrous compound (I).

The *ammonium* salt,  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CO{-}{-}{-}{-}C\cdot ONH_4}\\ \mathrm{CH(C_6H_4\cdot OH)\cdot C\cdot CO_2Et}\end{array}$, of the compound from salicylaldehyde, ethyl oxalacetate and ammonia, decomposes at 190°; the *copper* salt crystallises with $4H_2O$. The *ammonium* salt of the compound from anisaldehyde decomposes at 175°. The compound  $\mathrm{OH\cdot C_6H_3(OMe)\cdot CH}{<}\begin{array}{l}\mathrm{NH{-}{-}{-}CO}\\ \mathrm{CH(CO_2Et)\cdot CO}\end{array}$, prepared from vanillin, crystallises in rhombic prisms with $2H_2O$; the *ammonium* salt decomposes at 175°. The compound from piperonal gives an *ammonium* salt decomposing at 185°; the *copper* salt, $(C_{14}H_{12}NO_6)_2Cu,C_2H_4O_2$, forms yellowish-green needles.

Furfuraldehyde condenses with ethyl oxalacetate and ammonia to form the *compound*  $\mathrm{C_4OH_3\cdot CH}{<}\begin{array}{l}\mathrm{NH\cdot CH\cdot CO_2Et}\\ \mathrm{CO{-}CO}\end{array}$. From acetaldehyde, the *compound*  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CO{-}{-}CO}\\ \mathrm{CHMe\cdot CH\cdot CO_2Et}\end{array}$ (m. p. 146°) is obtained similarly; it is anhydrous and has a definite melting point, differing in these respects from all the other compounds of a similar type; a second form of this substance (m. p. 132°), also anhydrous, is produced with it, the two compounds being probably the racemic and meso-forms which should exist owing to the presence of two asymmetric carbon atoms. The *copper* salt crystallises with $1H_2O$.

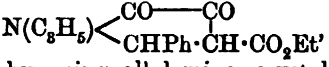
The *compound*  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CO{-}{-}{-}CO}\\ \mathrm{CH(C_6H_{13})\cdot CH\cdot CO_2Et}\end{array}$ (m. p. 128°), prepared from heptaldehyde, ethyl oxalacetate, and ammonia, is also anhydrous, melts without decomposing, and appears to exist in two forms; the *ammonium* salt, which decomposes at 146°, the *potassium*, and *silver* salts are crystalline.

Ethyl 2 : 3-*diketo*-5-*phenyl*-1-*methylpyrrolidine*-4-*carboxylate*,


$$\mathrm{NMe}{<}\begin{array}{l}\mathrm{CO{-}{-}CO}\\ \mathrm{CHPh\cdot CH\cdot CO_2Et}\end{array}$$

prepared from ethyl oxalacetate, benzaldehyde, and methylamine, crystallises in white needles, is anhydrous, decomposes at 162°, and gives a crystalline *methylamine* salt, $C_{14}H_5O_4N,NH_2Me$, which decomposes at 155°.

Ethyl 2 : 3-*diketo*-5-*phenyl*-1-*allylpyrrolidine*-4-*carboxylate*,


$$\mathrm{N(C_3H_5)}{<}\begin{array}{l}\mathrm{CO{-}{-}CO}\\ \mathrm{CHPh\cdot CH\cdot CO_2Et}\end{array}$$

prepared similarly by using allylamine, crystallises from alcohol in slender needles, m. p. 146°; the *allylamine* salt forms silky prisms and decomposes at 142°.

Ethyl 2 : 3-*diketo*-5-*phenyl*-1-*benzylpyrrolidine*-4-*carboxylate*, prepared by using benzylamine, crystallises in white needles, m. p. 190° with decomposition; the *benzylamine* salt, m. p. 140°, is crystalline.

Ethyl 2 : 3-diketo-1 : 5-diphenylpyrrolidine-4-carboxylate, obtained from ethyl oxalacetate, benzaldehyde, and aniline (compare Abstr., 1904, i, 812), is also formed when ethyl oxalacetate is left at the ordinary temperature in ethereal solution with benzylideneaniline. The *potassium* salt, $C_{19}H_{16}O_4NK,3\frac{1}{2}H_2O$, the *barium*, *copper*, and *silver* salts are described; it does not form a salt with aniline.

In the introduction to the paper, the relationship of the substances described with compounds containing the same fundamental nucleus is discussed at length. W. A. D.

2′- and 4′-Nitro-6′-methyl-α-stilbazole. Felix B. Ahrens and August Luther (*Ber.*, 1907, **40**, 3400—3406).—2′-*Nitro*-6-*methyl-α-stilbazole*, $C_{14}H_{12}O_2N_2$, obtained by heating *o*-nitrobenzaldehyde with 2 : 6-lutidine and zinc chloride at 180—190° for ten hours, crystallises from dilute alcohol in slender, pale yellow needles, m. p. 55—57°. The following salts have been prepared. *Hydrochloride*, $C_{14}H_{12}O_2N_2,HCl$, glistening needles, m. p. 235—275° (decomp.); *hydrobromide*, slender, yellow needles, m. p. 240—241° (decomp.); *hydriodide*, yellow plates, m. p. 198—199°; *nitrate*, pale yellow needles, m. p. 148—149°; *picrate*, $C_{20}H_{15}O_9N_5$, m. p. 227—228° (decomp.) after sintering at 210°; *mercurichloride*, $C_{14}H_{12}O_2N_2,HCl,HgCl_2$, m. p. 147—148°; *aurichloride*, m. p. 191—192°; *platinichloride*, yellow plates; *hydrogen sulphate*, yellow needles, m. p. 130—131°; *stannichloride*,

$$C_{14}H_{12}O_2H_2,HCl,SnCl_2,$$

yellow needles, m. p. 225—226°; $C_{14}H_{12}O_2N_2,HCl,ZnCl_2$, m. p. 195—196°; $C_{14}H_{12}O_2N_2,HCl,BaCl_2$, long, yellow needles decomposing at 238°.

The isomeric 4′-*nitro*-6-*methyl-α-stilbazole* crystallises from dilute alcohol in long needles, m. p. 131—132°. The salts prepared are: *hydrochloride*, $C_{14}H_{12}O_2N_2,HCl$, long yellow needles, m. p. 221—222°; *nitrate*, pale yellow plates, m. p. 162—163°; *platinichloride*, decomposes at 255°; *aurichloride*, m. p. 225—226°; *mercurichloride*, yellow needles.

When reduced with tin and hydrochloric acid, the *o*-nitro-compound yields 2′-*amino*-6-*methyl-α-stilbazole*, $C_{14}H_{14}N_2$, in yellow, glistening needles, m. p. 136—137°. This readily absorbs carbon dioxide from the air, yielding the *carbonate*, $(C_{14}H_{14}N_2)_2,H_2CO_3$, The *hydrochloride*, $C_{14}H_{14}N_2,2HCl$, crystallises in pale yellow plates, m. p. 234—235°; the *stannichloride*, $C_{14}H_{14}N_2,2HCl,2SnCl_2$, forms orange-coloured needles, m. p. 278°, and the *mercurichloride*, similar needles, m. p. 164°. The platinichloride has not been obtained in a crystalline form. The diazotised amino-compound yields an *azo-dye*, $C_{24}H_{18}ON_3K$, with an alkaline solution of β-naphthol; it crystallises from alcohol in red plates, m. p. 157—158°, and dyes wool or silk.

4′-*Amino*-5-*methyl-α-stilbazole* forms pale brown needles, m. p. 139—140°. The *hydrochloride* decomposes at 265°; the *mercurichloride* crystallises in reddish-brown needles, m. p. 260° (decomp.); the *stannichloride* forms brown needles, m. p. 188—189°. The *azo-dye*,

$$C_{24}H_{18}ON_3Na,$$

obtained from the diazotised base and an alkaline solution of β-naphthol, crystallises in dark reddish-brown plates, m. p. 248—249°, and dyes silk and wool red.

2′-Amino-6-methyl-α-stilbazole couples with diazotised sulphanilic acid in alkaline solution yielding a yellowish-brown *dye*,

$$C_{20}H_{17}O_3N_4SNa,$$

which is readily reduced to sulphanilic acid and *diamino*-6-*methyl*-α-*stilbazole*, $C_{14}H_{15}N_3$, the latter of which crystallises from dilute alcohol in long needles, m. p. 148—149°. The *hydrochloride*,

$$C_{14}H_{15}N_3,3HCl,$$

forms needles, m. p. 249—250° (decomp.). The *mercurichloride*,

$$C_{14}H_{15}N_3,3HCl,3HgCl_2,$$

crystallises in yellow needles, m. p. 179—180°; the *stannichloride* forms glistening yellowish-brown needles, m. p. 245—246° (decomp.).

The bisdiazo-derivative of the base couples with an alkaline solution of β-naphthol yielding a pale red *dye*, $C_{34}H_{23}O_2N_5Na_2$, which crystallises from alcohol in plates, m. p. 180—181°. With β-naphtholdisulphonic acid (R-acid), a brownish-red *dye*, $C_{34}H_{23}O_{14}N_5S_4Na_4$, is obtained; it crystallises from water in plates.

4′-Amino-6-methyl-α-stilbazole yields a *dye*, $C_{20}H_{17}O_3N_4SNa$, with diazotised sulphanilic acid; it crystallises from alcohol in yellowish-brown plates, and dyes silk, wool, and cotton yellow. 4′-Amino-α-stilbazole and diazotised sulphanilic acid yield a yellow *dye*,

$$C_{19}H_{15}O_3N_4SK,$$

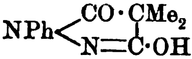
which can be reduced to sulphanilic acid and *diamino-α-stilbazole*,

$$C_{13}H_{13}N_3,$$

the latter of which crystallises in long, yellow needles, m. p. 126—127°. Its *hydrochloride*, $C_{13}H_{13}N_3,3HCl$, forms yellowish-red, glistening needles; its *mercurichloride*, red needles, and its *stannichloride*, long, red needles, m. p. 240—241°. J. J. S.

New Process for the Preparation of Aromatic 3-Hydroxy-5-pyrazolones or Pyrazolidones.

AUGUST MICHAELIS and KONRAD SCHENK (*Ber.*, 1907, **40**, 3568—3569).—Malonic acid and acetylphenylhydrazine condense in presence of phosphorus trichloride to 3-hydroxy-1-phenyl-5-pyrazolone previously described by Michaelis and Burmeister (Abstr., 1892, 1004). In a similar manner, dimethylmalonic acid condenses to 3-*hydroxy*-1-*phenyl*-4 : 4-*dimethyl*-5-*pyrazolone*,



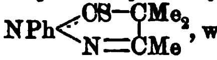
$$\mathrm{NPh}<\begin{matrix}\mathrm{CO\cdot CMe_2}\\ |\\ \mathrm{N{=}C\cdot OH}\end{matrix}$$

separating in colourless crystals, m. p. 176°.

Similarly, acetyl-*p*-bromophenylhydrazine and malonic acid condense to 3-*hydroxy*-1-p-*bromophenyl*-5-*pyrazolone*, crystallising in plates, m. p. 217°, and forming a red condensation product with benzaldehyde. The method appears to be generally applicable. E. F. A.

Thionpyrazolones.

RICHARD STOERMER and D. JOHANNSEN (*Ber.*, 1907, **40**, 3701—3703).—The action of phosphorus pentasulphide on pyrazolones yields thionpyrazolones and is therefore analogous to that on pyrrolidone (compare Tafel and Lawaczeck, this vol., i, 720).

The pyrazolone, obtained from ethyl dimethylacetoacetate, when heated at 140° with phosphorus pentasulphide yields 1-*phenyl*-3 : 4 : 4-*trimethyl*-5-*thionpyrazolone*,  $NPh<\begin{matrix}CS-CMe_2\\N=CMe\end{matrix}$, which crystallises in long, yellow prisms, m. p. 45—46°, b. p. 187—190°/12 mm. Methyl iodide gives a *dimethiodide*, m. p. 210—215°, which with silver chloride yields a *methochloride*, the *platinichloride* of which has m. p. 235—237°.

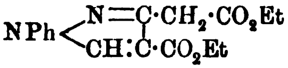
1-*Phenyl*-3-*methyl*-4 : 4-*diethyl*-5-*thionpyrazolone*, $C_{14}H_{18}N_2S$, yellow prisms, m. p. 80°, and 1-*phenyl*-3-*methyl*-5-*thionpyrazolone*, $C_{10}H_{10}N_2S$, of m. p. 109°, are best prepared in xylene solution. W. R.

Action of Phenylhydrazine on Ethyl Formylglutaconate.

WILHELM WISLICENUS and ERNST BREIT (*Annalen*, 1907, **356**, 32—44).—The action of phenylhydrazine on ethyl formylglutaconate has been again studied with the object of throwing light on certain points in the reaction left indefinite by the investigations of Wislicenus and Bindemann (Abstr., 1901, i, 361) and Hesse (*Diss.*, Würzburg, 1902). The first product of the reaction is now found to be an additive compound, $NHPh\cdot NH\cdot CH(CH_2\cdot CO_2Et)\cdot CH(CO_2Et)\cdot CHO$ or

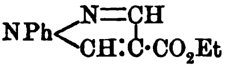
$$NHPh\cdot NH\cdot CH(CH_2\cdot CO_2Et)\cdot C(CO_2Et):CH\cdot OH.$$

This condenses, forming ethyl 1-phenylpyrazole-3-acetate-4-carboxylate (I) or ethyl 1-phenylpyrazole-4-carboxylate (II), depending on the conditions. The latter product is formed when the additive compound is heated in absence of air, which explains its formation on distillation of ethyl formylacetate-phenylhydrazone (*loc. cit.*):



$NPh<\begin{matrix}N=C\cdot CH_2\cdot CO_2Et\\CH:C\cdot CO_2Et\end{matrix}$

(I.)



$NPh<\begin{matrix}N=CH\\CH:C\cdot CO_2Et\end{matrix}$.

(II.)

The additive compound, $C_{16}H_{22}O_5N_2$, formed by mixing ethyl formylglutaconate and phenylhydrazine in cold ethereal solution, crystallises in needles, m. p. 70°, and on exposure to air in ethereal solution forms ethyl 1-phenylpyrazole-3-acetate-4-carboxylate, m. p. 89—90°. 1-*Phenylpyrazole*-3-*acetic*-4-*carboxylic acid*, $C_{12}H_{10}O_4N_2$, decomp. 221°, is formed by boiling the ester with aqueous baryta, evolves carbon dioxide on prolonged heating at 140°, forming 1-phenyl-3-methylpyrazole-4-carboxylic acid, and yields the ester, m. p. 89—90°, when boiled with alcoholic hydrogen chloride. The *barium*, $C_{12}H_8O_4N_2Ba,2H_2O$, and *silver*, $C_{12}H_8O_4N_2Ag_2$, salts were analysed.

When heated at 60—70° in presence of air, the additive compound yields a mixture of the above ester and ethyl 1-phenylpyrazole-4-carboxylate, m. p. 96—97°, together with ethyl acetate. In the absence of air, ethyl 1-phenylpyrazole-4-carboxylate and ethyl acetate only are formed.

When *p*-bromophenylhydrazine is added to an ethereal solution of ethyl formylglutaconate, the additive compound does not separate, but after some time the solution deposits *ethyl* 1-p-*bromophenylpyrazole*-3-*acetate*-4-*carboxylate*, $C_{16}H_{17}O_4N_2Br$, m. p. 128—129°, which does not give a coloration with potassium dichromate in concentrated sulphuric acid solution. But if the ethereal solution is rapidly evaporated, the additive compound separates, and if heated at 140° in a current of carbon dioxide, loses water and ethyl acetate forming *ethyl* 1-p-*bromophenylpyrazole*-4-*carboxylate*, $C_{12}H_{11}O_2N_2Br$, which crystallises in needles, m. p. 133—134°. G. Y.

The Hydrazones of Ethyl Formylacetate. WILHELM WISLICENUS and H. W. BYWATERS

(*Annalen*, 1907, **356**, 45—50. Compare preceding abstract; Wislicenus and Bindemann, Abstr., 1901, i, 361).—The phenylhydrazone of ethyl formylacetate yields the same condensation products as are obtained from the additive compound of phenylhydrazine and ethyl formylglutaconate.

Ethyl 1-phenylpyrazole-3-acetate-4-carboxylate is formed when the phenylhydrazone is treated with hydrogen chloride in cold absolute alcoholic solution, whilst ethyl 1-phenylpyrazole-4-carboxylate is obtained on distillation of the phenylhydrazone.

The p-*bromophenylhydrazone* of ethyl formylacetate, $C_{11}H_{13}O_2N_2Br$, crystallises in slightly yellow prisms, m. p. 80—81°, is more stable than the corresponding phenylhydrazone, and gives a dark violet coloration with concentrated sulphuric acid, or a brownish-red with alcoholic ferric chloride. On treatment with hydrogen chloride in absolute alcoholic solution, it condenses, forming ethyl 1-*p*-bromophenylpyrazole-3-acetate-4-carboxylate (preceding abstract), which distils in a vacuum with partial decomposition, and gives the pyrazoline reaction after reduction. 1-p-*Bromophenylpyrazole*-3-*acetic*-4-*carboxylic acid*, $C_{12}H_9O_4N_2Br$, crystallises in colourless needles, m. p. 229—230°; the *silver* salt, m. p. 270° (decomp.). When distilled in a vacuum, the *p*-bromophenylhydrazone of ethyl formylacetate yields ethyl 1-*p*-bromophenylpyrazole-4-carboxylate, m. p. 131—132°.

The *semicarbazone* of ethyl formylacetate, $C_6H_{11}O_3N_3$, crystallises in almost colourless prisms, m. p. 147—148°, and when heated at 160° in a sealed tube decomposes, forming alcohol, hydrazodicarbonamide, and a *resin*, which is soluble in alcohol and forms a *silver* salt.

G. Y.

Preparation of a *p*-Aminodiphenylaminesulphonic Acid. ERNST ERDMANN

(D.R.-P. 181179).—Although diphenylamine itself is not easily converted into a monosulphonic acid, one sulphonic group is readily introduced into the molecule of *p*-aminodiphenylamine, providing that the sulphuric acid contains a certain proportion of sulphur trioxide and that the sulphonation is effected at about 110—130°, the temperature required being dependent on the amount of trioxide present. The time required to complete the reaction varies from one to three hours. p-*Aminodiphenylaminesulphonic acid*, which is purified by dissolving in alkali and reprecipitating by mineral acid, is sparingly soluble in hot water, and crystallises from this solvent in clusters of fine needles. Its *sodium* and *potassium* salts crystallise from water, and the diazo-derivative separates as a yellow, crystalline product. The new acid differs from its isomerides in the coloration it furnishes with chromic acid and ferric chloride. G. T. M.

Preparation of Tetra-alkyldiaminodiphenylmethanesulphonic Acids. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 183793).—The direct sulphonation of tetramethyldiaminodiphenylmethane does not lead readily to the formation of a monosulphonic acid. The product is contaminated by coloured by-products and by substances of the sulphone type. It has now been found that the monosulphonic acids of this series may be synthesised in good yield by condensing formaldehyde with dimethyl- or diethyl-aniline and dimethylaniline-*m*-sulphonic acid.

Tetramethyldiaminodiphenylmethane-m-*sulphonic acid*,

$$NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_3(NMe_2)\cdot SO_3H,$$

crystallises from aqueous solutions, and its *sodium* salt may be salted out in the form of slender needles.

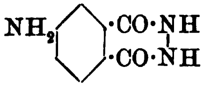
Dimethylaminodiethylaminodiphenylmethane-m-*sulphonic acid*,

$$NEt_2\cdot C_6H_4\cdot CH_2\cdot C_6H_3(NMe_2)\cdot SO_3H,$$

resembles its lower homologue. G. T. M.

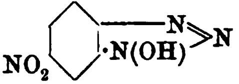
Action of Hydrazine Hydrate on Nitro-compounds. I. THEODOR CURTIUS (*J. pr. Chem.*, 1907, [ii], 76, 233—237).—A short account of the chief results of the study of the action of hydrazine hydrate on nitro-compounds previously unpublished or published only in dissertations.

Rothenberg showed (Abstr., 1893, i, 701) that whilst the action of hydrazine hydrate on oximes leads to substitution, *p*-nitrobenzene, *p*-nitrosodimethylaniline, and diphenylnitrosoamine are reduced by hydrazine hydrate forming aniline, *p*-aminodimethylaniline, and *as*-diphenylhydrazine respectively. It has since been found that the action of hydrazine hydrate on *p*-nitrosodimethylaniline leads also to the formation of traces of dimethylamine, whilst if the action is moderated by dilution of the hydrazine hydrate, tetramethyldiaminoazoxybenzene is formed.

Bollenbach (*Diss.*, Heidelberg, 1902), who obtained *o*- and *p*-aminophenols by reduction of the nitrophenols with hydrazine hydrate, was unable to reduce *m*- or *p*-nitrobenzoic acid in this manner, and found that *m*-dinitrobenzene is reduced only to *m*-nitroaminobenzene. On the other hand, Hoesch (*Diss.*, Heidelberg, 1904) has obtained *β-aminophthalhydrazide*,  by reduction of ethyl β-nitrophthalate by means of hydrazine hydrate.

The action of hydrazine hydrate on ethyl 3 : 5-dinitrobenzoate (Reidel, *Diss.*, Heidelberg, 1902; see following abstract) leads to the formation of 3 : 5-*dinitrobenzohydrazide*, which is reduced by an excess of hydrazine hydrate forming 3-*nitro*-5-*aminobenzohydrazide*. Similarly, 3 : 5-dinitrobenzoic acid forms the *hydrazine* salts of 3 : 5-dinitro- and 3-nitro-5-amino-benzoic acids. The second nitro-group, as in the case of *m*-dinitrobenzene, cannot be reduced in this manner.

Bollenbach (*loc. cit.*) found that 2 : 4-dinitrobenzoic acid reacts in analogous manner to hydrazine hydrate, forming 2-nitro-4-aminobenzoic acid. 2 : 4-Dinitrophenylhydrazine, on the contrary, is not reduced by hydrazine hydrate, which functions merely as an alkali, the reaction leading to the formation of 6-*nitro*-1-*hydroxy*-1 : 2 : 3-*benzotriazole*,



(Meyer, *Diss.*, Heidelberg, 1902). G. Y.

Action of Hydrazine Hydrate on Nitro-compounds. II. Action of Hydrazine Hydrate on Ethyl 3 : 5-Dinitrobenzoate.

THEODOR CURTIUS and ADOLF RIEDEL (*J. pr. Chem.*, 1907, [ii], 76, 238—263. Compare preceding abstract).—3 : 5-*Dinitrobenzohydrazide*, $C_6H_3(NO_2)_2\cdot CO\cdot NH\cdot NH_2$, prepared in a 63·7—69% yield by boiling ethyl 3 : 5-dinitrobenzoate with a limited amount of hydrazine hydrate in alcoholic solution, crystallises in yellow, prismatic needles, m. p. 158°, reduces ammoniacal silver nitrate and Fehling's solutions when heated, and forms crystalline condensation products with aldehydes and ketones. The crystalline *sodium* derivative,

$$C_6H_3(NO_2)_2\cdot CO\cdot NNa\cdot NH_2,$$

was analysed. The *benzylidene* derivative, $C_7H_4O_5N_2\colon CHPh$, crystallises in slightly brown needles, m. p. 262°. The *propylidene* derivative, $C_7H_4O_5N_2\colon CMe_2$, forms slightly yellow needles, m. p. 213·5°. The *acetyl* derivative, $C_6H_3(NO_2)_2\cdot CO\cdot NH\cdot NHAc$, crystallises in yellowish-white needles, m. p. 201·5°. When treated with sodium nitrite in glacial acetic acid solution, the hydrazide forms 3 : 5-*dinitrobenzoylazoimide*, $C_6H_3(NO_2)_2\cdot CO\cdot N_3$, which is obtained in small, white crystals, detonates slightly when heated, and yields 3 : 5-dinitrobenzoic acid when boiled with aqueous sodium hydroxide. 3 : 5-*Dinitrobenzanilide*, $C_{13}H_9O_5N_3$, formed by boiling the azoimide with aniline, crystallises in brown needles, m. p. 234°. *Ethyl* 3 : 5-*dinitrophenylcarbamate*, $C_6H_3(NO_2)_2\cdot NH\cdot CO_2Et$ (?), prepared by boiling the azoimide with absolute alcohol, is obtained as a viscid, red oil, which yields 3 : 5-dinitroaniline when boiled with concentrated hydrochloric acid. 3 : 5-*Dinitroacetanilide*, $C_8H_7O_5N_3$, crystallises in yellowish-white needles, m. p. 191°. The action of boiling methyl alcohol on the azoimide leads to the formation of methyl 3 : 5-dinitrobenzoate and azoimide. *s*-Bis-3 : 5-dinitrophenylcarbamide, m. p. 265°, formed together with 3 : 5-dinitroaniline by boiling 3 : 5-dinitrobenzoylazoimide with water, is probably identical with Struve and Radenhausen's tetranitrocarbanilide (Abstr., 1896, i, 35).

Bis-3 : 5-*dinitrobenzoylhydrazide*,

$$C_6H_3(NO_2)_2\cdot CO\cdot N_2H_2\cdot CO\cdot C_6H_3(NO_2)_2,$$

prepared by the action of iodine on 3 : 5-dinitrobenzoylhydrazide in boiling alcoholic solution, is obtained in a 30% yield as a yellow powder, m. p. 276°, and dissolves unchanged in concentrated sulphuric acid, being reprecipitated on addition of water. When heated with alcoholic hydrogen chloride at 100° in a sealed tube, it is decomposed, yielding *m*-dinitrobenzene and hydrazine. The crystalline *disodium* derivative, $N_2Na_2[CO\cdot C_6H_3(NO_2)_2]_2$, is described.

3-*Nitro*-5-*aminobenzoylhydrazide*, $NH_2\cdot C_6H_3(NO_2)\cdot CO\cdot NH\cdot NH_2$, is formed in a 60% yield together with a reddish-grey, crystalline *powder*, m. p. 283—284°, having the composition of bisdinitrobenzoylhydrazide, when ethyl 3 : 5-dinitrobenzoate is boiled in concentrated alcoholic solution with an excess of hydrazine hydrate. 3-Nitro-

5-aminobenzoylhydrazide is formed also by boiling ethyl 3-nitro-5-aminobenzoate with hydrazine hydrate in alcoholic solution. It crystallises in yellowish-red leaflets, m. p. 221°, and reduces ammoniacal silver nitrate and Fehling's solutions when heated.

Hydrazonium 3 : 5-*dinitrobenzoate*, $C_6H_3(NO_2)_2\cdot CO_2H,N_2H_4$, formed by heating 3 : 5-dinitrobenzoic acid with a limited amount of hydrazine hydrate in alcoholic solution, crystallises in yellowish-brown needles, m. p. 168°, reduces ammoniacal silver nitrate and Fehling's solutions in the cold, yields benzaldazine and 3 : 5-dinitrobenzoic acid when shaken with benzaldehyde in aqueous solution, and is converted into ethyl 3 : 5-dinitrobenzoate when heated with alcoholic hydrogen chloride.

Hydrazonium 3-*nitro*-5-*aminobenzoate*, $NH_2\cdot C_6H_3(NO_2)_2\cdot CO_2H,N_2H_4$, prepared by boiling 3 : 5-dinitrobenzoic acid or its hydrazonium salt with an excess of hydrazine hydrate in alcoholic solution, crystallises in reddish-yellow needles, m. p. 207° (decomp.), reduces ammoniacal silver nitrate and Fehling's solutions in the cold, and when shaken with benzaldehyde yields benzaldazine and 3-nitro-5-aminobenzoic acid.

The following substances derived from 3-nitro-5-aminobenzoylhydrazide are described. The *hydrochloride*, $C_7H_8O_3N_4,2HCl$, brown crystals, m. p. 221—222°. The *benzylidene* derivative, $C_{14}H_{12}O_3N_4$, yellow, prismatic needles, m. p. 247—248°. The m-*hydroxybenzylidene* derivative, $C_{14}H_{12}O_4N_4$, reddish-brown leaflets, m. p. 242°. The m-*nitrobenzylidene* derivative, $C_{14}H_{11}O_5N_5$, yellow needles, m. p. 240°. The *propylidene* derivative, $C_{10}H_{12}O_3N_4$, golden needles, m. p. 208°. The *triacetyl* derivative, $NHAc\cdot C_6H_3(NO_2)_2\cdot CO\cdot NAc\cdot NHAc$, yellow nodules, m. p. 256°. The *dibenzoyl* derivative,

$$NHBz\cdot C_6H_3(NO_2)_2\cdot CO\cdot NH\cdot NHBz,$$

slightly brown needles, m. p. 236°.

3-*Nitro*-5-*hydroxybenzoylazoimide*, $NO_2\cdot C_6H_3(OH)\cdot CO\cdot N_3$, prepared by the action of sodium nitrite on 3-nitro-5-aminobenzoylhydrazide in acetic acid solution, is obtained as a reddish-yellow, flocculent substance, which becomes brown when dried in a desiccator and detonates when heated. It dissolves in aqueous sodium hydroxide with slight evolution of gas, forming a dark red solution, and on addition of sulphuric acid yields azoimide. 3-*Nitro*-5-*hydroxybenzanilide*,

$$NO_2\cdot C_6H_3(OH)\cdot CO\cdot NHPh,$$

formed by boiling the azoimide with aniline, crystallises in white needles, m. p. 232°. The *urethane*, $NO_2\cdot C_6H_3(OH)\cdot NH\cdot CO_2Et$, formed by boiling the azoimide with absolute alcohol, is obtained as a viscid, red oil, and, when heated with sodium hydroxide and hydrogen chloride successively, yields 3-nitro-5-aminophenol.

When heated with water, 3-nitro-5-hydroxybenzoylazoimide forms s-*di*-3-*nitro*-5-*hydroxyphenylcarbamide*, $CO[NH\cdot C_6H_3(OH)\cdot NO_2]_2$, and small amounts of 3-nitro-5-aminophenol. The carbamide is obtained as a brittle mass, decomp. 260—270°, and is decomposed by boiling concentrated sodium hydroxide forming 3-nitro-5-aminophenol.

s-*Di*-3-*nitro*-5-*aminobenzoylhydrazide*, $N_2H_2[CO\cdot C_6H_3(NH_2)\cdot NO_2]_2$, prepared by boiling 3-nitro-5-aminobenzoylhydrazide with iodine in alcoholic solution, is obtained as a yellow, granular powder, m. p. 263—264°, and is hydrolysed, forming hydrazine, by alcoholic hydrogen chloride at 100°. G. Y.

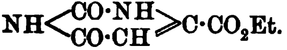
Preparation of 5 : 5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 183628).—The dialkylbarbituric acids are obtained by heating the dialkylmalonyldiurethanes, produced from the dialkylmalonyl chlorides and alkylurethanes, either alone or in the presence of carbamide, phenyl carbonate, or a similar compound.

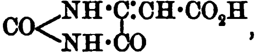
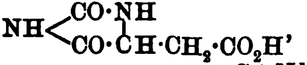
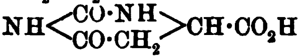
G. T. M.

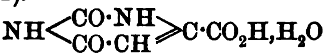
Preparation of 5 : 5-Dialkylbarbituric Acids. E. MERCK (D.R.-P. 183857).—The ethyl dialkylmalonates yield 5 : 5-dialkylbarbituric acids when heated either with biuret or an alkyl allophanate. Ethyl dialkylmalonates, when heated with either biuret or ethyl allophanate in alcoholic sodium ethoxide, furnish 5 : 5-dialkylbarbituric acids (compare Abstr., 1906, i, 461). G. T. M.

Preparation of 4 : 6-Dioxy-2-thio-5 : 5-dialkylpyrimidines. EMANUEL MERCK (D.R.-P. 182764).—4 : 6 - Dioxy - 2 - thio-5 : 5-diethylpyrimidine may be produced by heating diethylmalonyl chloride with thiocarbamide at 100°, and 4 : 6-dioxy-2-thio-5 : 5-dipropylpyrimidine is similarly prepared from dipropylmalonyl chloride. These substances are readily oxidised to the corresponding 5 : 5-dialkylbarbituric acids by dilute nitric acid or alkaline permanganate.

G. T. M.

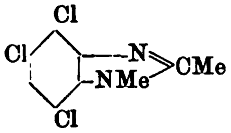
Pyrimidines. XXIII. Uracil-4-carboxylic Acid. HENRY L. WHEELER (*Amer. Chem. J.*, 1907, 38, 358—366).—By the condensation of carbamide with ethyl oxalacetate, Müller (Abstr., 1897, i, 549) obtained a compound which he regarded as ethyl uracil-4-carboxylate,  $NH<\begin{matrix}CO\cdot NH\\CO\cdot CH\end{matrix}>C\cdot CO_2Et$.

As no evidence was adduced to prove that the substance had this pyrimidine structure, it seemed possible that it might be the ester of the acid,  $CO<\begin{matrix}NH\cdot C{:}CH\cdot CO_2H\\NH\cdot CO\end{matrix}$, obtained by Gabriel (Abstr., 1906, i, 636) by the action of bromine on malylureide. Müller's ester has therefore been prepared and studied, and it has been found that on hydrolysis it yields an acid, which is not identical with Gabriel's acid, and on treatment with bromine is converted into dibromobarbituric acid. It is proved, therefore, that Müller's ester has the structure originally assigned to it, that Gabriel was right in concluding that his acid was not a pyrimidine, and that malylureide has the constitution,  $NH<\begin{matrix}CO\cdot NH\\CO\cdot CH\cdot CH_2\cdot CO_2H\end{matrix}$, proposed by Guareschi (Abstr., 1877, i, 458), and not  $NH<\begin{matrix}CO\cdot NH\\CO\cdot CH_2\end{matrix}>CH\cdot CO_2H$, as suggested by Grimaux (Abstr., 1875, 752).

Uracil-4-carboxylic acid,  $NH<\begin{matrix}CO\cdot NH\\CO\cdot CH\end{matrix}>C\cdot CO_2H,H_2O$, m. p. 347° (decomp.), crystallises from water in prisms; the *methyl* ester, m. p. 230°, forms colourless needles; the *potassium* and *barium* salts are described.

An attempt to prepare ethyl uracil-4-carboxylate by treating ethyl oxalacetate with ethyl-ψ-thiocarbamide hydrobromide resulted in the formation of an additive *compound*, $C_{11}H_{20}O_5N_2S$, m. p. 133—134°, which crystallises in colourless needles and when boiled with hydrochloric acid yields a *substance*, m. p. 206—207°, which contains sulphur, but not nitrogen. When ethyl cyanoacetylacetate is treated in the same way, an additive *compound*, $C_{10}H_{17}O_3N_3S$, m. p. 159°, is produced, which separates from alcohol in colourless, flat prisms. Ethyl oxalomalonate, under similar conditions, yields an additive *compound*, $C_{17}H_{32}O_7N_4S_2$, m. p. 181° (decomp.), which crystallises from alcohol in lustrous scales. E. G.

[Properties of Substituted Amidines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 180126).—The amidines derived from the aromatic orthodiamines may be employed as substitutes for camphor in the production of celluloid.



Methylbenziminazole, m. p. 113—115°, trichloro-2-methyl-1-ethylbenziminazole, m. p. 116—117° (from ethyl aceto-*o*-nitrotrichloroanilide), and 4 : 5 : 7-trichloro-1 : 2-dimethylbenziminazole, m. p. 120—121°, can be worked up with nitrocellulose in the presence of alcohol. G. T. M.

3-Amino-2-methylquinoline. O. STARK (*Ber.*, 1907, 40, 3425—3433).—When the oxime of 3-acetyl-2-methylquinoline is heated with sulphuric acid at 180°, the Beckmann reaction occurs, followed by hydrolysis, and the elimination of the acetyl group, and the final product is *3-amino-2-methylquinoline* : $C_9NH_5Me{\cdot}CMe{:}NOH \longrightarrow C_9NH_5Me{\cdot}NH{\cdot}COMe \longrightarrow C_9NH_5Me{\cdot}NH_2$.

A 92% yield of 3-acetyl-2-methylquinoline may be obtained by heating an alcoholic solution of *o*-aminobenzaldehyde and acetylacetone with a few drops of piperidine. It melts at 78—79° (compare Eliasberg and Friedländer, Abstr., 1892, 1106). The *semicarbazone*, $C_{13}H_{14}ON_4$, crystallises from alcohol in small, colourless needles, m. p. 208°.

3-Amino-2-methylquinoline crystallises from ether in long, yellow needles, m. p. 159—160°, or from light petroleum in brilliant golden needles. The *hydrochloride*, $C_{10}H_{10}N_2,2HCl$, obtained by passing dry hydrogen chloride into an absolute ethereal solution of the base, forms a yellowish-white, crystalline powder; the *platinichloride*, $2C_{10}H_{10}N_2,H_2PtCl_6,2H_2O$, forms glistening golden needles, and darkens when heated to 220—230°; the *picrate*, $C_{10}H_{10}N_2,C_6H_3O_7N_3$, also forms golden needles, and decomposes at about 235°. The *acetyl* derivative, $C_9NH_5Me{\cdot}NHAc$, crystallises from ether in needles, m. p. 164°. The solutions of the acetyl derivative do not fluoresce until hydrolysis has begun. The same acetyl derivative may also be obtained by the action of a phosphorus oxychloride solution of phosphorus pentachloride on the oxime.

When oxidised with permanganate, the aminomethylquinoline yields acetylanthranilic acid. 4-Hydroxy-2-methylquinoline crystallises from water with $2H_2O$, but if a solution of the compound saturated at 60—65° is boiled, anhydrous crystals separate. When reduced with hydrogen iodide in acetic acid solution, 3-amino-4-hydroxy-2-methylquinoline yields quinaldine (2-methylquinoline), and not aminoquinaldine as stated by Conrad, Limpach, and Eckhardt (Abstr., 1888, 1111). J. J. S.

Fluorescence of 3-Amino-2-methylquinoline and 3-Amino-4-hydroxy-2-methylquinoline. Use of 3-Amino-2-methylquinoline as an Indicator. O. STARK (*Ber.*, 1907, **40**, 3434).—Pure aqueous solutions of 3-amino-2-methylquinoline and of 3-amino-4-hydroxy-2-methylquinoline do not fluoresce even in very dilute solutions. The former compound fluoresces in acid solutions only, and the latter in both acid and alkaline solution, thus indicating the relationship between fluorescence and dissociation. A pure aqueous solution of the hydroxy-derivative is best obtained by distillation in steam; it is then non-fluorescent, but the addition of the minutest trace of acid on alkali produces fluorescence.

3-Amino-2-methylquinoline is an excellent indicator in acidimetry, and can replace methyl-orange. An alcoholic solution is the best to use. J. J. S.

Some Methineammonium Dyes. A. PORAI-KOSCHITZ [with P. SOLODOWINKOFF and M. TROITZKI] (*Zeitsch. Farb. Ind.*, 1907, **6**, 291—295. Compare Rupe and Porai-Koschitz, Abstr., 1906, i, 754; Nölting and Witte, *ibid.*, 886).—2-m-*Aminostyryl*-6-*methylquinoline*, $C_9NH_6Me{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NH_2$, prepared by reducing with stannous chloride and hydrochloric acid the corresponding nitro-compound prepared from *m*-nitrobenzaldehyde and 2:6-dimethylquinoline (Gasda, Abstr., 1906, i, 41), crystallises from benzene in slightly yellow needles, m. p. 160·5°, and gives a yellow *hydrochloride*, $C_{18}H_{16}N_2,2HCl$.

2-p-*Nitrostyryl*-6-*methylquinoline*, $C_9NH_6Me{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, prepared by condensing *p*-nitrobenzaldehyde with 2:6-dimethylquinoline, crystallises from pyridine as a bright green powder, m. p. 177°; its reduction gives 2-p-*aminostyryl*-6-*methylquinoline*, which crystallises from dilute alcohol in bright yellow leaflets, m. p. 173° after darkening at 164°; the *hydrochloride*, $C_{18}H_{16}N_2,HCl$, is purple-red, and the *benzoyl* derivative forms an orange, crystalline powder, m. p. 224°.

2-p-*Dimethylaminostyryl*-6-*methylquinoline*,

$$C_9H_6MeN{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NMe_2,$$

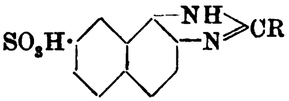
obtained from *p*-dimethylaminobenzaldehyde and 2:6-dimethylquinoline, crystallises from dilute alcohol or pyridine in long, yellow needles, m. p. 198°; the *hydrochloride*, $C_{20}H_{20}N_2,HCl$, is a purple, crystalline powder.

5-m-*Aminostyrylacridine*, $C_{13}NH_8{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NH_2$, prepared by reducing 5-*m*-nitrostyrylacridine (Friedländer, Abstr., 1905, i, 829) with stannous chloride and hydrochloric acid, crystallises from pyridine in short, yellow needles, m. p. 232—234°; its salts are vermilion-red.

5-p-*Nitrostyrylacridine*, prepared by heating *p*-nitrobenzaldehyde with 5-methylacridine and zinc chloride at 140—150°, crystallises from alcohol in small, bright yellow needles, m. p. 212°; its salts are sparingly soluble in water. 5-p-*Aminostyrylacridine*, obtained by reducing the foregoing, or by heating aminobenzaldehyde with 5-methylacridine and zinc chloride at 120°, crystallises from alcohol as a yellow powder, m. p. 209°. 5-p-*Dimethylaminostyrylacridine*, prepared by fusing *p*-dimethylbenzaldehyde with 5-methylacridine and zinc chloride during six hours at 135°, crystallises from alcohol; m. p. 238—239·5°; the *hydrochloride*, $C_{23}H_{20}N_2,HCl$, is blue; the *dihydrochloride*, yellow and unstable.

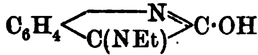
The foregoing *p*-aminobenzylidene compounds, derived from 6-methylquinaldine and 5-methylacridine, dye wool, silk, and mordanted cotton darker shades (orange to red) than the corresponding benzylidene compounds; on the other hand, the *m*-aminobenzylidene compounds either do not possess tinctorial properties or are only feebly yellow. W. A. D.

Preparation of 2-Derivatives of 6-Hydroxy-αβ-naphthiminazole-8-sulphonic Acid. Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 181178. Compare Abstr., 1906, i, 713).—



The naphthiminazole derivatives, derived from 1 : 2-diaminonaphthalene-5 : 7-disulphonic acid on fusion with alkali hydroxides, lose the sulphonic group in position 5, and become converted into 6-hydroxy-αβ-naphthiminazole-8-sulphonic acids having the annexed general formula. G. T. M.

Action of Ethylamine on Isatin. C. Haslinger (*Ber.*, 1907, **40**, 3598—3601. Compare this vol., i, 657).—Whilst the action of aromatic amines and diamines, and of pyrrole and piperidine on isatin, has been investigated exhaustively, of the aliphatic amines that of amylamine only has been studied (Schiff, *Annalen*, 1867, **144**, 53). Ethylamine is now found to react with dibromoisatin yielding a yellow, a colourless, and a green product, depending on the conditions of the reaction. Under similar conditions, isatin and bromoisatin yield each only a yellow and a colourless product. All three classes of compounds dissolve in concentrated sulphuric acid, the yellow compounds forming a red to reddish-violet, the green compound forming a blue, solution from which the corresponding isatin is precipitated on addition of water; the colourless compounds form colourless solutions and are reprecipitated unchanged on dilution. With fuming hydrochloric acid, the yellow compounds form red solutions, which slowly become orange-yellow and deposit the isatin; the blue compound gives the same reaction, but more slowly, whilst the colourless compounds remain undissolved.

3-*Ethyliminoisatin*, 
$C_6H_4{<}{\overset{N}{\underset{C(NEt)}{}}}{>}C{\cdot}OH$, prepared by treating isatin with an equal amount of 33% alcoholic ethylamine solution, crystallises in yellow needles and intumesces at 152°, forming a violet mass which dissolves in alcohol to a reddish-violet solution.

3 : 3-*Diethylamino*-1-*ethyl-ψ-isatin*, $C_6H_4{<}\begin{matrix}NEt\\C(NHEt)_2\end{matrix}{>}CO$, prepared by treating isatin with four times its weight of 33% alcoholic ethylamine solution, separates from ethyl acetate in white crystals and rapidly decomposes, losing ethylamine, in solution.

5-*Bromo-3-ethyliminoisatin*, $C_{10}H_9ON_2Br$, forms yellow crystals and intumesces at about 167°, forming a violet mass; the *potassium* derivative, $C_{10}H_8ON_2BrK$, crystallises in red needles.

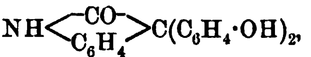
5 : 7-*Dibromo*-3-*ethyliminoisatin*, $C_{10}H_8ON_2Br_2$, is yellow, and decomposes about 175°.

5 : 7-*Dibromo*-3 : 3-*diethylamino*-1-*ethyl-ψ-isatin*, $C_{14}H_{19}ON_3Br_2$, forms white needles, and is stable towards solvents.

5 : 7-*Dibromo*-2-*ethylaminoisatin* (5 : 7-*dibromo*-2-*ethylimino-ψ-isatin*), $C_6H_4{<}\begin{matrix}N\\CO\end{matrix}{\geqslant}C\cdot NHEt$ or $C_6H_4{<}\begin{matrix}NH\\CO\end{matrix}{>}C{:}NEt$, prepared by prolonged action of an excess of ethylamine on dibromoisatin, forms green crystals.

Dichloroisatin yields the three corresponding derivatives with ethylamine. G. Y.

Oxidation of Phenolisatin. CARL LIEBERMANN and N. DANAILA (*Ber.*, 1907, 40, 3588—3597).—In connexion with the study of indigotin-like colouring matters from isatin (this vol., i, 657), the authors have investigated the constitution of the dye formed by oxidation of phenolisatin. Baeyer and Lazarus (Abstr., 1886, 155) showed phenolisatin to have the constitution



$$NH{<}\begin{matrix}CO\\C_6H_4\end{matrix}{>}C(C_6H_4\cdot OH)_2,$$

and considered the deep red dye formed by oxidation of this with potassium ferricyanide in alkaline solution to be aminobenzaurin, $NH_2\cdot C_6H_4\cdot C(C_6H_4\cdot OH){<}\begin{matrix}C_6H_4\\O\end{matrix}$. It is found now that this dye is 2-aminoaurin, $NH_2\cdot C_6H_3(OH)\cdot C(C_6H_4\cdot OH){<}\begin{matrix}C_6H_4\\O\end{matrix}$, only traces of aminobenzaurin being formed.

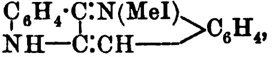
The name diphenolisatin is to be preferred to phenolisatin as more in agreement with the constitution. Diphenolisatin, m. p. 260—261° (220°: Baeyer and Lazarus, *loc. cit.*), forms stable *compounds* with ether, m. p. 70—80°, and chloroform, decomp. 110°. Contrary to Baeyer and Lazarus' statement, diphenolisatin forms a *triacetate*, $C_{20}H_{12}O_3NAc_3$, which separates from alcohol in white, microscopic crystals, m. p. 201—202°.

Halogenated diphenolisatins are prepared from halogenated isatins in the same manner as diphenolisatin from isatin. *Bromodiphenolisatin*, $NH{<}\begin{matrix}CO\\C_6H_3Br\end{matrix}{>}C(C_6H_4\cdot OH)_2$, crystallises in white needles, m. p. 235—236°, and forms a *triacetate*, $C_{20}H_{11}O_3NBrAc_3$, m. p. 217°. *Dibromodiphenolisatin*, $NH{<}\begin{matrix}CO\\C_6H_2Br_2\end{matrix}{>}C(C_6H_4\cdot OH)_2$, forms a *diacetate*, $C_{20}H_{11}O_3NBr_2Ac_2$, m. p. 237—238°. *Chlorodiphenolisatin*, m. p. 237—238°. Dichlorodiphenolisatin, m. p. 276—277°.

Diphenolisatins are oxidised to aminoaurins by potassium ferricyanide in alkaline solution or by potassium persulphate. The action of iodine on diphenolisation in alkaline solution leads to the formation of a bluer colour. The aminoaurins are obtained in orange, amorphous powders, insoluble in water or benzene, but readily soluble in cold alcohol or glacial acetic acid; the absorption bands in the spectra of the cherry-red, alkaline solutions lie nearer to the D line than those in the aurin spectrum. The coloration with concentrated sulphuric acid is redder with aminoaurin than with aurin.

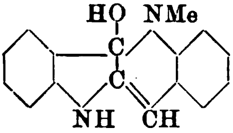
The following aminoaurins have been analysed: 2-*aminoaurin* (*isatin-red*), $C_{19}H_{15}O_3N$; 5-*bromo*-2-*aminoaurin*, $C_{19}H_{14}O_3NBr$; 3 : 5-*dibromo*-2-*aminoaurin*, $C_{19}H_{13}O_3NBr_2$; 5-*chloro*-2-*aminoaurin*, $C_{19}H_{14}O_3NCl$; *dichloro*-2-*aminoaurin*, $C_{19}H_{13}O_3NCl_2$. G. Y.

Methylquindolanol. FRIEDRICH FICHTER and HANS PROBST (*Ber.*, 1907, **40**, 3478).—It was shown by Fichter and Boehringer (this vol., i, 92) that, when quindoline methiodide,



$$\begin{array}{l} C_6H_4\cdot C{:}N(MeI) \\ NH—C{:}CH \end{array}\!\!>C_6H_4,$$

is treated with sodium hydroxide, it forms a ψ-base, *methylquindolanol*, which, it is now found, has the annexed formula; it crystallises from methyl alcohol in tiny needles. The application of the Zeisel method showed that no methoxy-groups were present. A. McK.



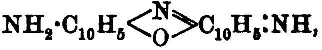
Preparation of Aromatic Monoacetyltriamines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 183843).—The aromatic monoacetyltriamines have hitherto not been obtained by the reduction of aromatic 2 : 4-dinitroacylamines owing to the resultant condensation between the contiguous amino- and acylamino-groups leading to the production of the anhydro-bases of the iminoazole series. It has now been found that reduction without condensation can be effected by the use of mild reducing agents, such as iron and dilute acetic or mineral acids.

4-*Acetylamino*-m-*phenylenediamine*, $NHAc\cdot C_6H_3(NH_2)_2$, prismatic crystals, m. p. 158—159°, results from the mild reduction of 2 : 4-dinitroacetanilide; when heated above its melting point or when boiled with glacial acetic acid, it loses water, forming aminomethylbenziminazole.

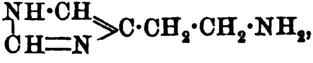
2-*Acetylamino*-3 : 5-*tolylenediamine*, $NHAc\cdot C_6H_2Me(NH_2)_2$, yellow needles, m. p. 210—211°, is less soluble than the preceding base, and is obtained from 3 : 5-dinitroaceto-*o*-toluidide in a similar manner. Favourable results are obtained by substituting these new bases for the ordinary meta-diamines in the production of azo-dyes.

G. T. M.

[Preparation of Triaminotriphenylethylene.] GEORGES IMBERT and CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 180011).—Trichloro- or tribromo-ethylene or acetylene tetrachloride, or the corresponding tetrabromide, when mixed with aniline and heated with a solution of alkali hydroxide or carbonate, furnishes an excellent yield of triaminotriphenylethylene, a base which is of use in pharmaceutical chemistry and the colour industry. G. T. M.

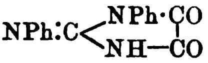
Oxazine Dyes. RUDOLF NIETZKI and VICTOR BECKER (*Ber.*, 1907, **40**, 3397—3400).—1 : 4-Diamino-2-naphthol forms a stable *hydrochloride*, $C_{10}H_{10}ON_2,2HCl$, which attacks the mucous membrane. The free base rapidly turns brown on exposure to the air. A blue oxazine dye, *diaminonaphthoxazone*,  $NH_2\cdot C_{10}H_5<\overset{N}{\underset{O}{}}>C_{10}H_5{:}NH$, is obtained when an alcoholic solution of this hydrochloride is boiled with crystallised sodium acetate while a current of air is passed through the solution. It forms well-developed, glistening crystals. A crystalline *hydrochloride*, $C_{20}H_4ON_3Cl$, is formed when the base is dissolved in phenol, precipitated with alcohol and hydrochloric acid, and dried at 100°. It dyes cotton mordanted with tannin, and its alcoholic and acetic acid solutions exhibit a brilliant red fluorescence. When the aminosulphonic acid, known as eikonogen, is used in place of the diaminonaphthol, a *disulphonic acid* derivative of the above dye is obtained.

1 : 4-Diamino-β-naphthol-6-sulphonic acid yields a *diaminonaphthoxazonedisulphonic acid*, which dyes wool in an acid-bath a blue colour. J. J. S.

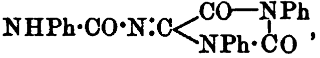
Synthesis of Iminoazolylethylamine [4-β-Aminoethylglyoxaline]. ADOLF WINDAUS and W. VOGT (*Ber.*, 1907, **40**, 3691—3695).—The recognition that glyoxaline radicles are contained in the alkaloid pilocarpine (Jowett, Trans., 1903, **83**, 438) and in substances derived from proteins like histidine (Pauly, Abstr., 1904, i, 1068) has suggested the synthesis of these natural products. As a step in this direction, glyoxaline-4-propionic acid (Abstr., 1905, i, 834) has been converted into 4-β-*aminoethylglyoxaline*,  $\begin{matrix}NH\cdot CH\\ CH{=}N\end{matrix}>C\cdot CH_2\cdot CH_2\cdot NH_2$, by means of Curtius' method.

Ethyl glyoxalinepropionate is a colourless oil, obtained by esterification and purification by means of the *oxalate*, which crystallises in rhombic plates, m. p. 158° ; the *picrolonate* forms light yellow needles, m. p. 226° (decomp.). The *hydrazide*, $C_6H_{10}ON_4$, obtained by the interaction of the ester and 50% hydrazine hydrate, has m. p. 142°. The *hydrochloride* of aminoethylglyoxaline is obtained in 55% yield by treating an alcoholic solution of the hydrazide with amyl nitrite and hydrochloric acid to form the azoimide, decomposing this to obtain the urethane, and finally hydrolysing the urethane. It crystallises in prisms, m. p. 240° (decomp.). No sparingly soluble salts are given by ammoniacal zinc or silver hydroxides in contradistinction to other glyoxaline compounds. The *platinichloride* is orange, blackens towards 200°, but does not melt ; *picrate*, m. p. 239° (decomp.) ; *picrolonate* is characteristic, m. p. 266° (decomp.).

By treating the aminoethylglyoxaline with benzoyl chloride and sodium hydroxide, the ring is ruptured and *tribenzoylbutenetriamine*, $\mathrm{NHBz\cdot CH{:}C(NHBz)\cdot[CH_2]_2\cdot NHBz}$, is obtained as glistening needles, m. p. 191°. W. R.

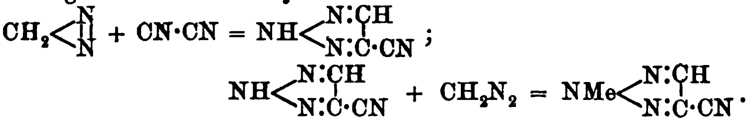
Behaviour of Hydrogen Cyanide towards Phenylcarbimide. II. WALTER DIECKMANN and HEINRICH KÄMMERER (*Ber.*, 1907, **40**, 3737—3743. Compare Abstr., 1905, i, 874).—By the action of sodium ethoxide, diphenylparabanimide is converted into the isomeric as-*oxalyldiphenylguanidine*,  $\mathrm{NPh{:}C}<\begin{array}{l}\mathrm{NPh\cdot CO}\\ \quad\ \ |\\ \mathrm{NH-CO}\end{array}$, m. p. 225°, which forms colourless prisms, has acid properties, and is hydrolysed by concentrated hydrochloric acid yielding aniline and *phenylparabanic acid*, m. p. 209—210°. The two new compounds are also obtained by the condensation of ethyl oxalate with diphenylguanidine and phenylcarbamide respectively in the presence of sodium ethoxide.

Melanoximide (*s*-oxalyldiphenylguanidine), m. p. 225°, which is obtained most conveniently by warming diphenylguanidine cyanide with dilute acetic acid, is also converted by sodium ethoxide into *as*-oxalyldiphenylguanidine.

With phenylcarbimide at 120°, diphenylparabanimide yields the *carbanilide*,  $\mathrm{NHPh\cdot CO\cdot N{:}C}<\begin{array}{l}\mathrm{CO-NPh}\\ \quad\ \ |\\ \mathrm{NPh\cdot CO}\end{array}$, m. p. 233°, which is therefore the final product of the action of hydrogen cyanide on phenylcarbimide (*loc. cit.*). By prolonged heating with glacial acetic acid, the carbanilide yields diphenylparabanic acid, whereas hydrolysis by a mixture of hydrochloric and glacial acetic acids forms in addition phenylcarbamide.

Phenylcarbamide is hydrolysed by boiling acetic acid yielding diphenylcarbamide and small quantities of aniline and acetanilide; by dilute hydrochloric acid giving ammonium chloride, aniline hydrochloride, and carbon dioxide, and by boiling water forming diphenylcarbamide, ammonia, aniline, and carbon dioxide. C. S.

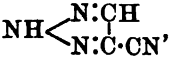
Action of Diazo-derivatives of Aliphatic Hydrocarbons on Cyanogen and its Derivatives. I and II. Cyanogen. ALBERTO PERATONER and E. AZZARELLO (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 237—243; 318—328. Compare Azzarello, Abstr., 1905, i, 867).—An ethereal solution of cyanogen reacts violently with a 2—5% ethereal solution of diazomethane or diazoethane, forming a cyano-derivative of osotriazole, which, unless special precautions are taken, undergoes etherification by the diazomethane:

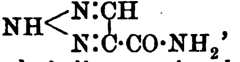


$$\mathrm{CH_2}<\begin{array}{l}\mathrm{N}\\ \|\\ \mathrm{N}\end{array} + \mathrm{CN\cdot CN} = \mathrm{NH}<\begin{array}{l}\mathrm{N{:}CH}\\ \quad\ |\\ \mathrm{N{:}C\cdot CN}\end{array};$$

$$\mathrm{NH}<\begin{array}{l}\mathrm{N{:}CH}\\ \quad\ |\\ \mathrm{N{:}C\cdot CN}\end{array} + \mathrm{CH_2N_2} = \mathrm{NMe}<\begin{array}{l}\mathrm{N{:}CH}\\ \quad\ |\\ \mathrm{N{:}C\cdot CN}\end{array}.$$

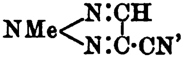
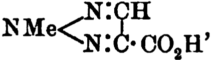
In order to prevent the etherification, a very small amount of the diazo-compound must be treated with a large excess of cyanogen in cold ethereal solution. The fact that only one of the CN groups in the cyanogen molecule reacts with the diazo-hydrocarbon, no compound consisting of two triazole nuclei joined by their carbon atoms being formed, would indicate a structure other than $\mathrm{N{\vdots}C{\cdot}C{\vdots}N}$ for cyanogen. The balance of evidence, which the authors review, is, however, in favour of the above formula.

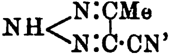
3-*Cyano-osotriazole*,  $\mathrm{NH}{<}\begin{array}{l}\mathrm{N{:}CH}\\ \mathrm{N{:}C{\cdot}CN}\end{array}$, separates from benzene in small, white crystals, m. p. 113—114°, and gives precipitates with salts of many heavy metals. The corresponding *amide*,

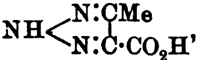


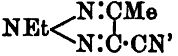
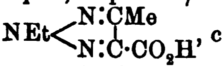
$$\mathrm{NH}{<}\begin{array}{l}\mathrm{N{:}CH}\\ \mathrm{N{:}C{\cdot}CO{\cdot}NH_2}\end{array},$$

prepared by the action of alcoholic potassium hydroxide on the cyano-compound, is deposited from alcohol in small, white crystals, m. p. 256—257°. When treated with 40% alcoholic potassium hydroxide solution, or with concentrated hydrochloric acid, it yields the osotriazolecarboxylic acid described by Baltzer and von Pechmann (Abstr., 1891, 1116), and this, when heated at 230—240°, is converted into the osotriazole prepared by these authors.

3-*Cyano*-1-*methylosotriazole*,  $\mathrm{NMe}{<}\begin{array}{l}\mathrm{N{:}CH}\\ \mathrm{N{:}C{\cdot}CN}\end{array}$, is a colourless, neutral liquid, b. p. 95°/30 mm., having a fruity odour. When heated with 40% alcoholic potassium hydroxide, it is converted quantitatively into the potassium derivative of 1-*methylosotriazole*-3-*carboxylic acid*,  $\mathrm{NMe}{<}\begin{array}{l}\mathrm{N{:}CH}\\ \mathrm{N{:}C{\cdot}CO_2H}\end{array}$, which is deposited from acetone or benzene in small, white crystals, m. p. 141—142°. The *potassium*, $C_4H_4O_2N_3K$, *barium*, $(C_4H_4O_2N_3)_2Ba,3\frac{1}{2}H_2O$, and *calcium* salts, and the *ethyl ester*, $C_2N_3HMe{\cdot}CO_2Et$, b. p. 115°/60 mm., were prepared.

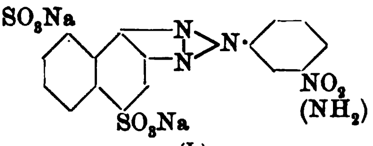
4-*Cyano*-3-*methylosotriazole*,  $\mathrm{NH}{<}\begin{array}{l}\mathrm{N{:}CMe}\\ \mathrm{N{:}C{\cdot}CN}\end{array}$, separates from benzene in small, white crystals, m. p. 84°, b. p. 160°/30 mm., has the normal molecular weight in freezing acetic acid, and, in aqueous solution, has an acid reaction. The *silver* derivative, $C_4H_3N_4Ag$, is a white powder stable towards light.

3-*Methylosotriazole*-4-*carboxylic acid*,  $\mathrm{NH}{<}\begin{array}{l}\mathrm{N{:}CMe}\\ \mathrm{N{:}C{\cdot}CO_2H}\end{array}$, separates from water in shining, acicular crystals, m. p. 214° (decomp.); the *calcium* salt, $(C_4H_4O_2N_3)_2Ca$, was prepared.

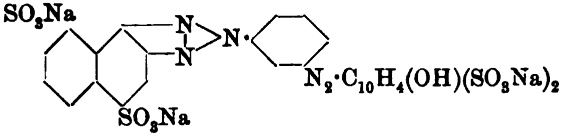
4-*Cyano*-3-*methyl*-1-*ethylosotriazole*,  $\mathrm{NEt}{<}\begin{array}{l}\mathrm{N{:}CMe}\\ \mathrm{N{:}C{\cdot}CN}\end{array}$, is an oily, neutral liquid, b. p. 105°/28 mm. 3-*Methyl*-1-*ethylosotriazole*-4-*carboxylic acid*,  $\mathrm{NEt}{<}\begin{array}{l}\mathrm{N{:}CMe}\\ \mathrm{N{:}C{\cdot}CO_2H}\end{array}$, crystallises from benzene in shining, white needles, m. p. 131°; its *calcium* salt, $(C_6H_8N_3O_2)_2Ca$, was prepared.

T. H. P.

[3′-Aminophenyl-αβ-naphthatriazole-5 : 9-sulphonic Acid.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 174548).—*Sodium-3′-nitrophenyl-αβ-naphthatriazole-5 : 9-sulphonate*,



(I.)



(II.)

(I) was prepared by coupling *m*-nitrodiazobenzene chloride with α-naphthylamine-3:8-disulphonic acid in sodium carbonate solution, and then, after 20 hours, warming the liquid to 70—75° and adding aqueous sodium hypochlorite. The product was salted out and reduced with iron filings and water acidified with hydrochloric acid; the solution was rendered alkaline with sodium carbonate and 3-aminophenyl-αβ-naphthatriazole-4 : 9-disulphonic acid (I) precipitated from the filtrate by adding hydrochloric acid and sodium chloride. The *azo*-derivative (II), obtained by coupling the aminotriazole with β-naphthol-3 : 6-disulphonic acid, when dissolved in water and treated with a solution of barium chloride and a paste of aluminium hydroxide, yields a brilliant reddish-lake which is remarkably stable to light. G. T. M.

The Mechanism of the Indamine and Azine Synthesis. Willstätter's Paper on Aniline-Black. Hans Th. Bucherer (*Ber.*, 1907, 40, 3412—3419. Compare this vol., i, 641).—The syntheses of indamines, azines, thiazines, and oxazines are represented by a single scheme, based on the two following facts. (1) The readiness with which *o*- and *p*-diamines, -aminophenols, dihydroxy-derivatives, and the corresponding sulphur compounds are oxidised. (2) The readiness with which monoimines, di-imines, quinols, and the corresponding sulphur compounds form additive compounds. In addition, attention is drawn to the readiness with which groups attached to nitrogen, oxygen, or sulphur wander into the nucleus. The two reactions, which occur alternately in the case of a *p*-diamine, may be represented as (*a*) *p*-diamine + O ⟶ *p*-di-imide and (*b*) *p*-di-imide + HX ⟶ *p*-diamine with the X group attached to nitrogen.

Several examples are worked out in detail, more especially the formation of safranine, methylene-blue, and Meldola's blue. Also the formation of 2 : 2′-diaminoazobenzene from *o*-quinonedi-imine and of diaminoazodiphenyl from the oxidation product of benzidine.

Willstätter's formula for aniline-black is criticised. J. J. S.

Action of Hydroxylamine on Safranones. Otto Fischer and Fritz Römer (*Ber.*, 1907, 40, 3406—3411. Compare Fischer and Arntz, this vol., i, 94; Kehrmann and Prager, *ibid.*, 447).—Kehrmann and Prager's view of the constitution of the amino*iso*rosindone, obtained by the action of hydroxylamine on *iso*rosindone, is confirmed, since the ethers obtained by the action of alkyl iodides and potassium hydroxide on the corresponding hydroxy*iso*rosindone are not identical with the ethers of naphthasafranol. The ortho-position of the methoxy-group in the methyl ether has been established by the synthesis of the ether from nitrosoguaiacol and β-phenylnaphthylamine.

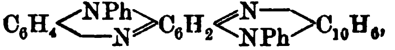
It appears that only those safranones yield amino-derivatives with hydroxylamine which are free from substituents in the two ortho-positions with respect to the quinone oxygen. Thus rosindone, *o*-methoxy*iso*rosindone, and β-*o*-methyl*iso*rosindone (Abstr., 1901, i, 417) do not yield amino-derivatives.

Safranol does not yield an amino-derivative with hydroxylamine, but safranol ethyl ether yields *o-aminosafranol ethyl ether*, $C_{20}H_{17}O_2N_3$, which crystallises from alcohol in brilliant brown plates, m. p. about 250°. The addition of concentrated hydrochloric acid to the alcoholic or acetic acid solution produces a yellowish-green coloration. The corresponding *methyl ether* is less soluble in alcohol.

o-Anilinoisorosindone, $C_{28}H_{19}ON_3$, obtained by heating *o*-amino*iso*rosindone with aniline and aniline hydrochloride at 150°, crystallises from alcohol in bronze-coloured needles, m. p. 282—284°.

A *naphthafluorindine*, $C_6H_4<\substack{NH\\N}>C_6H_2<\substack{N-\\NPh}>C_{10}H_6$, is obtained when *o*-amino*iso*rosindone, *o*-phenylenediamine, and its hydrochloride are heated with ethyl alcohol at 140—150° for three hours; it crystallises from pyridine in golden-bronze, glistening plates, which dissolve in glacial acetic acid yielding a pure blue solution. The same product is formed when *iso*rosindone is used instead of its amino-derivative, and even more readily from *iso*rosinduline salts and *o*-phenylenediamine (compare Fischer and Hepp, Abstr., 1896, i, 323).

o-Amino*iso*rosindone, or *iso*rosindone, when heated with *o*-aminodiphenylamine, its hydrochloride, and absolute alcohol at 150° for four hours, yields a green naphthafluorindine *derivative*,



$$C_6H_4<\substack{NPh\\N}>C_6H_2<\substack{N-\\NPh}>C_{10}H_6,$$

which crystallises from dimethylaniline in prisms.

Amino*iso*rosindone, or *iso*rosinduline, and *o*-naphthylenediamine also yield a green dye. These naphthafluorindine dyes exhibit but little fluorescence except in concentrated sulphuric acid or pyridine solutions (compare Nietzki and Vollenbruck, Abstr., 1904, i, 1062). J. J. S.

Disulphides with Neighbouring Double Linkings. Action of Amines and Hydrazines on Thiourets. New Synthesis of Triazoles. II. EMIL FROMM & EMIL VETTER (*Annalen*, 1907, 356, 178—196. Compare Fromm, Abstr., 1906, i, 656; Fromm and Schneider, *ibid.*, 656, 714; Hantzsch and Wolvekamp, Abstr., 1904, i, 719).—Perthiocyanic acid and thiouret undergo analogous reactions with potassium hydroxide, yielding sulphur and potassium cyanoaminodithiocarbonate and phenyliminocyanoaminothiocarbonate respectively. The present work was undertaken to determine if thiouret reacts with aniline and phenylhydrazine in a manner analogous to the reaction of perthiocyanic acid with these reagents, which leads to the formation of phenyldithiobiuret and derivatives of triazole respectively.

When heated with aniline on the water-bath in absence of a solvent, phenylthiouret hydrochloride yields thiocarbanilide, but if the reaction is moderated by dilution of the mixture with alcohol, sulphur and *phenylguanidophenylthiocarbamide*, $\mathrm{NHPh{\cdot}CS{\cdot}NH{\cdot}C(NPh){\cdot}NH_2}$, are formed. This crystallises in white leaflets, m. p. 197°, forms a crystalline *hydrochloride*, $\mathrm{C_{14}H_{14}N_4S,HCl}$, m. p. 179°, and on treatment with benzyl chloride and alcoholic sodium hydroxide yields the *benzyl* derivative, $\mathrm{C_{21}H_{20}N_4S}$, m. p. 157°.

The constitution of the products of the action of amines on thiouret hydrochlorides is confirmed by the formation of isomeric substances from phenylthiouret hydrochloride and *p*-phenetidine, on the one hand, and from *p*-phenetylthiouret hydrochloride and aniline, on the other, since if the products of the reaction had the constitution

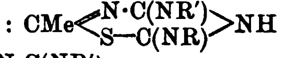
$$\mathrm{NHR{\cdot}C(NR'){\cdot}NH{\cdot}C(SH){:}NH},$$

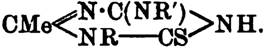
these two combinations would yield the same substance.

p-*Phenetylguanidophenylthiocarbamide*, $\mathrm{C_{16}H_{18}ON_4S}$, formed from phenylthiouret hydrochloride and *p*-phenetidine, crystallises in leaflets, m. p. 168°, and forms a *benzyl* derivative, $\mathrm{C_{23}H_{24}ON_4S}$, m. p. 230°.

The action of *p*-phenetidine on perthiocyanic acid leads to the formation of p-*phenetyldithiobiuret*, $\mathrm{C_{10}H_{13}ON_3S_2}$, crystallising in leaflets, m. p. 178°, and *di*-p-*phenetylthiocarbamide*, $\mathrm{C_{17}H_{20}O_2N_2S}$, crystallising in leaflets, m. p. 170°.

p-*Phenetylthiouret hydrochloride*, $\mathrm{C_{10}H_{11}ON_3S_2,HCl,H_2O}$, m. p. 137°, reacts with aniline, forming *phenylguanido*-p-*phenetylthiocarbamide*, m. p. 170°. This yields a *benzyl* derivative, $\mathrm{C_{23}H_{24}ON_4S}$, crystallising in leaflets, m. p. 166°.

The arylguanidoarylthiocarbamides form acetyl derivatives, $\mathrm{NHR{\cdot}CS{\cdot}NH{\cdot}C(NR'){\cdot}NHAc}$, which are converted by the action of alkalis into anhydro-compounds :  $\mathrm{CMe}{<}\begin{matrix}\mathrm{N{\cdot}C(NR')}\\ \mathrm{S{-}C(NR)}\end{matrix}{>}\mathrm{NH}$ or



$$\mathrm{CMe}{<}\begin{matrix}\mathrm{N{\cdot}C(NR')}\\ \mathrm{NR{-}CS}\end{matrix}{>}\mathrm{NH}.$$

Acetylphenylguanidophenylthiocarbamide, R and R′ = Ph, m. p. 240° ; the *anhydro*-compound, needles, m. p. 200° ; when heated with benzyl chloride and potassium hydroxide, it forms the benzyl derivative of phenylguanidophenylthiocarbamide. *Acetyl*-p-*phenetylguanidophenylthiocarbamide*, m. p. 183° ; the *anhydro*-compound, m. p. 204°. *Acetylphenylguanido*-p-*phenetylthiocarbamide*, needles, m. p. 172° ; the *anhydro*-compound, m. p. 187°.

When heated with phenylhydrazine in alcoholic solution, phenylthiouret hydrochloride forms sulphur and *anilguanidophenylthiocarbamide*, $\mathrm{NPh{:}C(SH){\cdot}NH{\cdot}C(NH){\cdot}NH{\cdot}NHPh}$ or perhaps

$$\mathrm{NH{:}C(SH){\cdot}NH{\cdot}C(NPh){\cdot}NPh{\cdot}NH_2},$$

which separates from alcohol in crystals, m. p. 167°, and if heated with alcoholic sodium hydroxide or dilute hydrochloric acid yields 3-amino-5-anilino-1-phenyltriazole or its hydrochloride (Fromm and Göncz, this vol., i, 372). The filtrate from the preparation of anilguanidophenylthiocarbamide contains a small amount of an *isomeride*,

$$\mathrm{NHPh{\cdot}NH{\cdot}C(NPh){\cdot}NH{\cdot}C(NH){\cdot}SH}$$

or $\mathrm{NH_2{\cdot}NPh{\cdot}C(NH){\cdot}NH{\cdot}C(NPh){\cdot}SH}$, which on successive treatment with sodium hydroxide and hydrochloric acid yields 5-amino-3-anilino-1-phenyltriazole hydrochloride (Fromm and Göncz, *loc. cit.*).

Anilguanido-p-*phenetylthiocarbamide*, $\mathrm{C_{16}H_{19}ON_5S}$, m. p. 168°

(decomp.), when boiled with sodium hydroxide in alcoholic solution, yields 3-*amino*-5-p-*phenetidino*-1-*phenyltriazole,* $C_{16}H_{17}ON_5$, m. p. 134°; the *hydrochloride* of this, $C_{16}H_{17}ON_5,HCl$, crystallises in thin leaflets, m. p. 66°. The *acetyl* derivative, $C_{20}H_{23}O_3N_5,H_2O$, crystallises in needles, m. p. 145—148°.

Aminophenylguanido-p-*phenetylthiocarbamide,* $C_{16}H_{19}ON_5S$, obtained from the mother-liquor from the preparation of its isomeride, crystallises in white leaflets, m. p. 236°, and when treated successively with sodium hydroxide and hydrochloric acid yields 5-*amino*-3-p-*phenetidino*-1-*phenyltriazole hydrochloride,* m. p. 175°, which is sparingly soluble. The free *triazole* forms a gelatinous mass and is readily soluble in alcohol. G. Y.

isoPurone. Julius Tafel and Percy Alfred Houseman (*Ber.*, 1907, 40, 3743—3751. Compare Tafel, Abstr., 1901, i, 236).—The products obtained by the electrolytic reduction of uric acid are treated with concentrated ammonium hydroxide to separate the tetrahydrouric acid, with sodium hydroxide to remove *iso*purone, and the residue yields purone by crystallisation from hot water. *iso*Purone is an unsaturated substance which can be estimated by iodine and thiosulphate. The molecular weights of purone and of *iso*purone determined in aqueous solution by the ebullioscopic method correspond with the formula $C_5H_8O_2N_4$.

iso*Tetrahydrouric acid,* $C_5H_8O_3N_4$, prepared by the action of bromine on an aqueous solution of *iso*purone at 0°, crystallises in colourless needles, decomposes at 200°, has a neutral reaction, and dissolves readily in alkalis. A boiling solution of barium hydroxide converts it into the yellow *barium* salt of α-*iso*uracil, $C_4H_6O_4N_2Ba$, from which careful treatment with 2*N*-hydrochloric acid at −10° liberates α-iso*uracil,* $C_4H_4O_2N_2$. This substance crystallises in needles, decomposes at 350°, has an acid reaction, dissolves in dilute alkalis, decolorises bromine water, and gives a violet-brown coloration with ferric chloride.

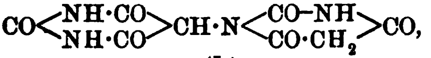
The mother-liquor from which the barium salt of α-*iso*uracil has been precipitated contains β-iso*uracil,* $C_4H_4O_2N_2$, which crystallises in slender needles, has a neutral reaction, dissolves in dilute alkalis, and forms a crystalline substance with phenylhydrazine which seems to be a hydrazone. C. S.

Reduction of Theophylline and Paraxanthine. Julius Tafel and Julius Dodt (*Ber.*, 1907, 40, 3752—3757. Compare Abstr., 1900, i, 121).—The electrolytic reduction of theophylline in 30% sulphuric acid at the ordinary temperature, with prepared lead cathodes and a current density of 12 amperes per sq. dcm., results in the formation of *deoxytheophylline,* $C_7H_{10}ON_4$, which separates from hot water in crystals containing $3H_2O$, darkens at 200° and has m. p. 215—225°, has a faintly alkaline reaction, and is soluble in dilute acids or alkalis; the *hydrochloride* and the *picrate* are mentioned. By the action of bromine in cold glacial acetic acid, the substance yields *bromodeoxytheophylline,* $C_7H_9ON_4Br$, which is converted by sodium hydroxide into 6-*hydroxydeoxytheophylline,* $C_7H_{10}O_2N_4,2H_2O$.

Analogous compounds are obtained from paraxanthine by similar treatment. *Deoxyparaxanthine*, $C_7H_{10}ON_4$, crystallises from water with $1H_2O$, decomposes at 250°, has a neutral reaction, and is not more soluble in dilute alkalis than in water. *Bromodeoxyparaxanthine*, $C_7H_9ON_4Br$, dissolves in water to a strongly acid solution, and is converted by sodium hydroxide into 6-*hydroxydeoxyparaxanthine*, $C_7H_{10}O_2N_4,2H_2O$, which darkens at 230°. C. S.

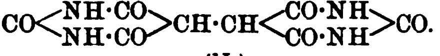
Acidity of Deoxyxanthines. JULIUS TAFEL and JULIUS DODT (*Ber.*, 1907, **40**, 3757—3759. Compare preceding abstract).—It has been shown that deoxyxanthine, 3-methyldeoxyxanthine, and deoxytheophylline, unlike deoxyheteroxanthine, deoxyparaxanthine, and deoxytheobromine, are more soluble in dilute alkalis than in water. The authors have measured the strengths of these compounds by Wood's method (Trans., 1906, **89**, 1839) and arrive at the conclusions that the deoxyxanthines are weaker acids than the xanthines, and that in the deoxyxanthines the acid properties are conferred solely by the glyoxaline ring. C. S.

Hydurilic Acid. MAX CONRAD (*Annalen*, 1907, **356**, 24—31).—Two constitutions have been ascribed to hydurilic acid (I and II). The author shows that the constitution II is the correct one. Since barbituric acid when heated with concentrated hydrochloric acid is hydrolysed forming carbon dioxide, ammonia, and acetic acid, an acid of the constitution II must under the same conditions yield carbon dioxide, ammonia, and succinic acid. It is found that when heated with concentrated hydrochloric acid at 200—230°, hydurilic acid yields succinic acid in almost quantitative amount.



$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CH\cdot N}\left<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO\cdot CH_2}\end{matrix}\right>\mathrm{CO},$$

(I.)

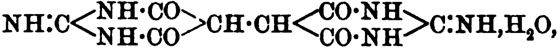


$$\mathrm{CO}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CH\cdot CH}\left<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\right>\mathrm{CO}.$$

(II.)

The constitution II is supported also by the formation of hydurilic acid by condensation of ethyl ethanetetracarboxylate with carbamide by means of alcoholic sodium ethoxide at 60—70°, and together with small amounts of succinic acid by hydrolysis of ethanetetracarbonylguanide by means of dilute hydrochloric acid at 150°.

Ethanetetracarbonylguanide,



$$\mathrm{NH{:}C}\left<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}\right>\mathrm{CH\cdot CH}\left<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\right>\mathrm{C{:}NH,H_2O},$$

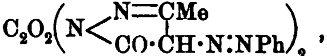
is prepared in a 63% yield by heating ethyl ethanetetracarboxylate with guanidine hydrochloride and sodium ethoxide in alcoholic solution at 70°; it crystallises in needles, decomp. when heated, is readily soluble in alkali hydroxides or carbonates, separates in prisms on prolonged heating of its ammoniacal solution, and dissolves in cold nitric acid. The *silver* salt, $C_8H_6O_4N_6Ag_2,\frac{1}{2}H_2O$, was analysed; the *hydrochloride* crystallises in white needles. Ammonium hydurilate gives a green coloration with ferric chloride, becoming colourless on addition of hydrochloric acid or on heating, and forms a red solution with potassium nitrite in acetic acid. G. Y.

Azo-derivatives of Esters of Bis-β-ketonic Acid Oxalyldihydrazones. CARL BÜLOW [and, in part, MARTIN LOBECK] (*Ber.*, 1907, **40**, 3787—3798).—The two methylene groups in ethyl oxalylbishydrazoneacetoacetate (Bülow and Lobeck, this vol., i, 301) are capable of reacting, like the methylene group in compounds of the type $COR''\cdot NH\cdot N{:}CR'\cdot CH_2\cdot CO_2R$, with diazobenzene chloride with the formation of *o*-azoacylhydrazones. These azo-derivatives are, generally speaking, far more stable than the parent substances.

Ethyl oxalyldihydrazone-benzeneazobisacetoacetate,
$CO_2Et\cdot CH(N{:}NPh)\cdot CMe{:}N\cdot NH\cdot CO\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et$,
obtained by the action of diazobenzene chloride on ethyl oxalylbishydrazoneacetoacetate in alcoholic solution in the presence of sodium acetate at low temperatures, crystallises in yellow, felted needles, m. p. 155° (unsharp); at the same time, is formed a small quantity of *ethyl oxalylbishydrazonebenzeneazoacetate*,

$$C_2O_2[NH\cdot N{:}CMe\cdot CH(N{:}NPh)CO_2Et]_2.$$

The latter compound alone is produced by using very dilute solutions, but is better prepared by the interaction of oxalylhydrazide and ethyl benzeneazoacetoacetate in alcoholic or acetic acid solution. It forms colourless crystals, swells and froths up at 211—212° or 217—218°, and decomposes slightly above this temperature into alcohol and 1 : 1-*oxalylbis*-4-*benzeneazo*-3-*methyl*-5-*pyrazolone*,



$$C_2O_2\left(N<\begin{matrix}N{=}CMe\\ CO\cdot CH\cdot N{:}NPh\end{matrix}\right)_2,$$

obtained as a yellowish-red, crystalline powder, m. p. 256—257°. This compound is decomposed by hot potassium hydroxide solution or pyridine into oxalic acid and 4-benzeneazo-3-methyl-5-pyrazolone (compare von Rothenburg, Abstr., 1895, i, 686).

Ethyl oxalylbishydrazonebenzeneazoacetoacetate is decomposed on boiling with phenylhydrazine in acetic acid solution with the formation of alcohol, oxalylhydrazide, and 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone.

The author replies to the criticisms of Curtius, Darapsky, and Müller (this vol., i, 451). W. H. G.

Action of Diazobenzene Chloride on *p*-Hydroxybenzoic Acid. EUGEN GRANDMOUGIN and H. FREIMANN (*Ber.*, 1907, **40**, 3453—3454. Compare Limpricht, Abstr., 1891, 1036).—Diazobenzene chloride reacts with a solution of *p*-hydroxybenzoic acid in the presence of sodium carbonate, yielding bisbenzeneazophenol together with a small amount of benzeneazo-*p*-hydroxybenzoic acid (Auwers and Röhrig, Abstr., 1897, i, 341). In the presence of sodium hydroxide, the chief product is trisbenzeneazophenol (this vol., i, 664).

J. J. S.

Preparation of 1-Diazo-β-naphtholdi- and tri-sulphonic Acids. KALLE & Co. (D.R.-P. 184477).—The 1-amino-β-naphtholmonosulphonic acids are diazotised normally with sodium nitrite in the presence of organic acids (Abstr., 1905, i, 161); the corresponding di- and tri-sulphonic acids are readily converted into diazo-derivatives in the presence of sulphuric acid, provided that dilute solutions are employed at 0° to 5°. The diazo-derivatives may be partially salted out from the yellowish-brown solution in the form of a brown mass.

G. T. M.

[The Diazotisation of 1-Amino-β-naphtholsulphonic Acids.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 181714).—The interaction of nitrous acid and the 1-amino-β-naphtholsulphonic acids leads to the production of quinonoid substances, so that the reaction is largely one of oxidation. If, however, the sodium salts of these 1-amino-β-naphtholsulphonic acids are acetylated in the hydroxyl group with acetic anhydride, then the acetyl derivatives thus obtained furnish yellow, crystalline diazo-compounds, such as 2-acetoxy-1-diazonaphthalene-4-sulphonic acid, which, on treatment with dilute aqueous alkalis, lose their acetyl group and give rise to the corresponding 2-hydroxy-1-diazonaphthalenesulphonic acids. This elimination of acetyl may be effected similarly after combining the 2-acetoxy-1-diazonaphthalenesulphonic acid with phenol and aromatic amines, and in this way 2-hydroxyazonaphthalene colouring matters are produced which may be employed as mordant dyes. G. T. M.

Bisazo-derivatives of Salicylic Acid. EUGEN GRANDMOUGIN, J. R. GUISAN, and H. FREIMANN (*Ber.*, 1907, **40**, 3450—3453. Compare Limpricht, Abstr., 1891, 1036).—A mixture of bisbenzeneazosalicylic acid, benzeneazosalicylic acid, and the trisazo-derivative of phenol (this vol., i, 664) is formed when a solution of diazobenzene chloride and salicylic acid dissolved in sodium hydroxide is kept at 0° for some five days. The monoazo-compound remains dissolved in the alkaline solution, and may be precipitated by the addition of acid. The *bisbenzeneazosalicylic acid*, $OH\cdot C_6H_2(N_2Ph)_2\cdot CO_2H$, may be extracted with hot dilute sodium hydroxide solution, and crystallises from chloroform in reddish-brown, felted needles, m. p. 218°. With sulphuric acid, it gives the colorations characteristic of bisazo-compounds, and when reduced with stannous chloride yields 3 : 5-diaminosalicylic acid.

The *acetyl* derivative of the bisazo-compound has m. p. 196°. *Bis-o-tolueneazosalicylic acid*, $C_{21}H_{18}O_3N_4$, forms dark violet crystals with a metallic lustre, m. p. 170°, and yields an *acetyl* derivative, m. p. 173°. *o-Tolueneazosalicylic acid*, $C_{14}H_{12}O_3N_2$, forms yellowish-brown needles, m. p. 191°, and yields an *acetyl* derivative, m. p. 145°.

Tris-o-tolueneazophenol, $C_{27}H_{22}ON_6$, forms bronze-coloured needles, m. p. 198°, and its *acetyl* derivative orange-coloured needles, m. p. 195°. Diazotised nitroanilines yield monoazo-derivatives together with bisazo-derivatives of phenol.

Bis-p-nitrobenzeneazophenol, $C_{18}H_{12}O_5N_6$, crystallises from nitrobenzene or tetrachloroethane in brown, felted needles, and its *acetyl* derivative has m. p. 208°. J. J. S.

Aromatic - aliphatic - *p* - aminoazo - compounds. WALTHER BORSCHE and A. RECLAIRE (*Ber.*, 1907, **40**, 3806—3815).—The condensation products of quinoneoximes and semicarbazides (compare Borsche, Abstr., 1906, i, 319) are converted on reduction with tin and hydrochloric acid and subsequent oxidation, into aromatic-aliphatic-*p*-aminoazo-compounds of the type $NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NHR$, corresponding with the quinonemonosemicarbazones,

$$OH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NHR.$$

The reduction of either *p*-nitrophenylsemicarbazide (Hyde, Abstr., 1899, i, 688) or benzoquinoneoximesemicarbazone (Thiele and Barlow, Abstr., 1899, i, 47) with tin and hydrochloric acid results in the formation of p-*aminophenylsemicarbazide* (p-*aminobenzenehydrazoformamide*) *hydrochloride*, colourless leaflets, decomposing at 195—196°; ammonia liberates the free *base*, $NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, as small, colourless needles, which rapidly oxidise in the air. A solution of the hydrochloride on treatment with potassium cyanate and sodium acetate deposits pearly, white leaflets of p-*carbamidophenylsemicarbazide*,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

m. p. 201—202° (decomp.). Benzaldehyde reacts with the base with the formation of *benzylidene*-p-*aminophenylsemicarbazide*,

$$CHPh{:}NH{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

yellowish-white leaflets, m. p. 204° (decomp.).

p-*Aminobenzeneazoformamide*, obtained only in the form of a hydrate, $NH_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH_2,H_2O$, is prepared by the oxidation of the hydrazo-compound; it crystallises in dark red needles with a blue reflex, m. p. 125—126° (decomp.). The molecule of water is not removed by keeping the compound some days in a vacuum desiccator. It is converted by strong hydrochloric acid into a greenish-yellow *hydrochloride*, and is decomposed on heating with potassium hydroxide solution according to the equation: $NH_2{\cdot}C_6H_4{\cdot}N_2{\cdot}CO{\cdot}NH_2 + 2KOH = NH_2Ph + N_2 + NH_3 + K_2CO_3$; at the same time, a small quantity of a *substance* is formed, which crystallises in brown needles. p-*Carbamidobenzeneazoformamide*, $NH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH_2,H_2O$, prepared by acting on a solution of the hydrazo-compound with ammonia and hydrogen peroxide, crystallises in small, brick-red needles, m. p. 178° (decomp.).

Phenylcarbamido-p-*aminobenzeneazoformamide*,

$$NHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH_2,$$

which results from the interaction of phenylcarbimide and the azo-compound, crystallises in yellowish-red needles, decomposing at 202°.

Benzoyl-p-*aminobenzeneazoformamide*, $NHBz{\cdot}C_6H_4{\cdot}N{:}N{\cdot}CO{\cdot}NH_2$, forms small, orange needles, m. p. 218° (decomp.). Bromine acts on the parent azo-compound yielding 3 : 5(?)-*dibromo*-4-*aminobenzeneazoformamide*, $NH_2{\cdot}C_6H_2Br_2{\cdot}N_2{\cdot}CO{\cdot}NH_2$, small, yellow needles, m. p. 183°.

2-*Toluquinoneoxime*-5-*semicarbazone*,

$$OH{\cdot}N{:}C_6H_3Me{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

prepared by the interaction of 2-toluquinoneoxime and semicarbazide hydrochloride, is a brown, crystalline powder, decomposing at 220°. It yields, on reduction with tin and hydrochloric acid and subsequent oxidation of the hydrazo-compound, 2-*aminotoluene*-5-*azoformamide*, $NH_2{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}CO{\cdot}NH_2,H_2O$, small, reddish-brown needles, m. p. 85—86° (decomp.). In the same way, are obtained 3-*toluquinone*-

oxime-6-*semicarbazone*, small, brown needles, decomposing at 243°, and 2-*thymoquinoneoxime*-5-*semicarbazone*,

$$OH\cdot N{:}C_6H_2MePr^{\beta}{:}N\cdot NH\cdot CO\cdot NH_2,$$

small, yellow needles, m. p. 221—222°, which also give rise to amino-azo-compounds.

Phenylcarbimide combines with the three nitrophenylhydrazines, forming o-*nitrobenzenehydrazoformanilide*,

$$NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot CO\cdot NHPh,$$

small, slender, yellow needles, m. p. 220°; m-*nitrobenzenehydrazoformanilide*, yellow leaflets, m. p. 220°, and p-*nitrobenzenehydrazoformanilide*, small, yellowish-white needles, m. p. 220°. Both the latter compound and benzoquinoneoximephenylsemicarbazone (Borsche and Kühl, Abstr., 1906, i, 320) yield on reduction with tin and hydrochloric acid p-*aminobenzenehydrazoformanilide hydrochloride*, small, colourless, slender needles, which decompose and turn violet above 190°; sodium carbonate liberates the free *base*, $NH_2\cdot C_6H_4\cdot NH\cdot NH\cdot CO\cdot NHPh$, long, colourless needles, m. p. 187° (decomp.), which is converted on oxidation into p-*aminobenzeneazoformanilide*,

$$NH_2\cdot C_6H_4\cdot N{:}N\cdot CO\cdot NHPh,$$

large, blood-red leaflets, m. p. 160—161° (decomp.). The salts of the latter compound with acids are stable only in the presence of the free acid; *hydrochloride*, small, orange-yellow needles; *oxalate*,

$$C_{13}H_{12}O_4N_4,C_2H_2O_4,$$

dark brown, crystalline powder, decomposing at 186—187°. The following compounds were also prepared: *benzoyl* derivative,

$$NHBz\cdot C_6H_4\cdot N_2\cdot CO\cdot NHPh,$$

small, yellow needles, m. p. 219—220°; *phenylcarbamido*-derivative, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot CO\cdot NHPh$, reddish-yellow needles, decomposing at 210°; *dibromo*-derivative, $NH_2\cdot C_6H_2Br_2\cdot N_2\cdot CO\cdot NHPh$, small, yellow needles, m. p. 155—156°.

By the same methods as described above are obtained: 2-*aminotoluene*-5-*azoformanilide*, $NH_2\cdot C_6H_3Me\cdot N{:}N\cdot CO\cdot NHPh$, reddish-brown, leafy crystals, decomposing at 150—151°, and 3-*aminotoluene*-6-*azoformanilide*, dark red needles with green reflex, m. p. 137°.

W. H. G.

Action of Dilute Sulphuric Acid on Proteins. Leo Langstein (*Biochem. Zeitsch.*, 1907, 5, 410—412).—Recent authors have stated that the digestion of protein with 0·5% hydrochloric acid leads to the formation of the same end products as are found in gastric digestion, but more slowly. The present experiments confirm earlier views of the author that protein is very resistant to dilute sulphuric acid. After eight months' digestion in 1% acid at 37°, only 18% of dried egg-albumin goes into solution; rather more of the other proteins investigated (serum-albumin, &c.) were dissolved. The dissolved nitrogenous substances were completely precipitable by phosphotungstic acid.

W. D. H.

Influence of Solutions of Pigments on the Heat Coagulation of Proteins. Hans Aron (*Biochem. Zeitsch.*, 1907, 5, 413—418).—Acid pigments (eosin and aurantia) or their free acids, when added to protein solutions (dilute serum), destroy the heat-coagulability of the latter. The explanation advanced is that complex colloid is formed, in which the pigment acts towards the protein as a "protective colloid." W. D. H.

Dissociation of Serum-Globulin at Varying Hydrogen Ion Concentrations. T. Brailsford Robertson (*J. Physical Chem.*, 1907, 11, 437—460. Compare Abstr., 1906, ii, 828; Hardy, Abstr., 1906, i, 121).—Equations are deduced by means of which an expression containing the ratio of the acid and basic constants, k_a and k_b, of such an amphoteric electrolyte as serum-globulin can be calculated from two experimental observations. The hydrogen ion concentrations of globulin solutions containing varying proportions of acid were measured by means of concentration cells and the conductivities of globulin solutions to which varying proportions of acid had been added were also measured; from these data, by an indirect method, the value $68{\cdot}3 \times 10^{-8}$ was obtained for the expression Kk_a/k_b, where K is the dissociation constant for water. By another and probably less accurate method, the value 265×10^{-8} was obtained for the same expression. For the velocity of the serum-globulin ion, the value 7×10^{-5} cm./sec. under a potential gradient of 1 volt/cm. was deduced, whilst Hardy (*loc. cit.*) by a direct method obtained 10×10^{-5} cm./sec.

Serum-globulin is a fairly strong acid, but its basic properties are so slight that it behaves to alkalis as a non-amphoteric acid.

Some evidence has been obtained that solutions of proteins contain more or less complex polymerides of the type HXOH, and that the equilibrium is displaced by the addition of acids, salts, &c. In the case of serum-globulin, therefore, there is no definite molecular concentration in acid solution, but in alkaline solution, owing to its slightly basic character, the degree of polymerisation and therefore the molecular weight is constant. The molecular weight of serum-globulin in alkaline solution is given as 1967, and the average molecular weight in acid solution as 1684, but the latter value is very uncertain. G. S.

Formation of Polypeptides by the Hydrolysis of Proteins. Emil Fischer and Emil Abderhalden (*Ber.*, 1907, 40, 3544—3562). In part already published (this vol., i, 737. Compare also 1906, i, 718).—When treated with 70% sulphuric acid at 36°, gliadin gives rise to *l*-leucyl-*d*-glutamic acid, $[\alpha]_D^{20}$ +10·2, m. p. 232° (corr.), identical with the synthetical product. Levene's claim to have first isolated a dipeptide from the decomposition products of proteins is shown to be inaccurate. E. F. A.

Hydrolysis of Glycinin, the Globulin of the Soy Bean, and of the Crystalline Globulin of the Squash Seed (Cucurbita maxima). Thomas B. Osborne and Samuel H. Clapp (*Amer. J. Physiol.*, 1907, 19, 468—474, 475—481).—Acid hydrolysis led to the following percentage results calculated on a moisture and ash-free basis for the two proteins mentioned:

	Soy bean.	Squash seed.		Soy bean.	Squash seed.
Glycine.........	0·97	0·57	Serine.........	not isolated	not isolated
Alanine.........	not isolated	1·92	Tyrosine ...	1·86	3·07
Valine	0·68	0·26	Arginine.....	5·12	14·44
Proline	3·78	2·82	Histidine ...	1·39	2·63
Phenylalanine	3·86	3·32	Lysine.........	2·71	1·99
Aspartic acid	3·89	3·30	Ammonia ...	2·56	1·55
Glutamic acid	19·46	12·35	Tryptophan	present	present
Leucine	8·45	7·32	Cystine	—	0·23

W. D. H.

The Formation of Acetone from Acetoacetates by means of Organ-extracts and Proteins. Leo Pollak (*Beitr. chem. Physiol. Path.*, 1907, 10, 232—250).—By digestion of sodium acetoacetate with blood-serum or organ-extracts, there is a rapid decomposition of the salt, with the formation of carbon dioxide and acetone. The agent in the serum responsible for this is protein. Serum-globulin, crystalline serum-albumin, caseinogen, Witte's peptone, amino-acids (leucine, alanine, &c.) all have the same action. All these substances contain the amino-group. W. D. H.

Combining Power of Casein with Certain Acids. John H. Long (*J. Amer. Chem. Soc.*, 1907, **29**, 1334—1342).—In previous papers (Abstr., 1905, i, 498; 1906, i, 391), it has been shown that casein unites with alkalis to form salts. It has now been found that casein also combines with acids, and the behaviour of various acids has been investigated. At the ordinary temperature, 1 gram of dry casein unites with nearly 7 c.c. of *N*/10 hydrochloric, hydrobromic, hydriodic, sulphuric, and acetic acids. It also combines with tartaric, phosphoric, and oxalic acids, but not with boric acid. If the casein solution is evaporated in presence of dilute acid, a larger quantity of the latter, in the case of hydrochloric acid, four times as much, enters into combination. This is due, to some extent at least, to the partial hydrolysis of the casein and the union of the acid with the products of such hydrolysis. E. G.

Action of Dilute Acids on Casein when Soluble Compounds are not Formed. Lucius L. Van Slyke and Donald D. Van Slyke (*Amer. Chem. J.*, 1907, **38**, 383—456).—In a previous paper (Abstr., 1905, i, 499), it has been shown that casein unites with acids to form insoluble products. A study has now been made of the behaviour of casein with hydrochloric, sulphuric, lactic, and acetic acids of concentrations from *N*/125 to *N*/2000, at temperatures of 0°, 25°, and 45°, and during periods varying from five minutes to forty-eight hours. The results indicate that the insoluble substances formed are not salts, but are produced by adsorption of the acid by the casein. The precipitate produced when milk turns sour is casein containing adsorbed lactic acid.

In carrying out the investigation, casein was shaken with dilute acids of known strength, and, after filtration, the quantity of acid removed from the solution was calculated from the decrease in conductivity. Experiments were made to ascertain the conditions in which casein is soluble in dilute acids in order that such conditions might be avoided. It was found that the protein does not dissolve to an appreciable extent when left for several hours at 0° in contact with acids of concentration of *N*/1000 or less, but that the solubility increases with the concentration, the temperature, and the time of contact. The rate at which casein dissolves in different acids of equivalent strength is not proportional to the concentration of the hydrogen ions or to the degree of dissociation, but is disproportionately great for the weak organic acids. From dilute acids of equal concentration, the dissolved protein takes up a larger proportion of acid than the undissolved. The solubility of casein in dilute acids is probably due to decomposition of the protein. Casein neither dissolves in *N*/125 magnesium sulphate or *N*/50 potassium chloride nor adsorbs either of these salts.

The amount of acid withdrawn by casein from dilute solutions in which it does not dissolve varies with the concentration of the acid, the duration of contact until equilibrium is reached, the degree of agitation until equilibrium is reached, the temperature, and the particular acid employed. The acid is never entirely removed from the solution.

Determinations have been made of the amount of each of the acids adsorbed by 1 gram of casein at the equilibrium point and of the rate at which equilibrium is produced under different conditions. The acid can be removed from the casein by shaking it with water.

E. G.

Sulphohæmoglobin. T. WOOD CLARKE and W. H. HARTLEY (*J. Physiol.*, 1907, **36**, 62—67).—Sulphohæmoglobin is regarded as a definite compound in aqueous solution. It could not be obtained in crystalline form. The action of carbon monoxide on sulphohæmoglobin, or of hydrogen sulphide on carboxyhæmoglobin, is to form a new compound, carboxysulphohæmoglobin. Reduction of oxyhæmoglobin is a necessary preliminary for the formation of sulphohæmoglobin. Selenohæmoglobin closely resembles sulphohæmoglobin.

W. D. H.

Hair Pigment, Choroid Pigment, and other Melanins. EDUARD SPIEGLER (*Beitr. chem. Physiol. Path.*, 1907, **10**, 253—264).—The pigment of melanotic livers is different from that of the hair, but both resemble the choroid pigment (from pigs' eyes) in not yielding hæmopyrrole, and so their origin from the blood is impossible. On decomposition of the pigments, acetone derivatives or condensation products of acetone residues are found; the differences between these products in the various pigments, accounts for the differences of the pigments. The parent substances of the pigments are tryptophan and acetone; possibly other aromatic groups of the protein molecule, such as phenylalanine and tyrosine, participate in their formation.

W. D. H.

The Chemical Nature of the Fundamental Colouring Matter of Urine. S. Dombrowski (*Compt. rend.*, 1907, **145**, 575—577).—The yellow urinary colouring matter, *urochrome*, has been prepared and examined. It may be separated from fresh urine which has been freed from most of its salts by the addition of cupric acetate in a cold faintly acid medium. The analytical data are: C, 43·09; H, 5·14; N, 11·15; S, 5·09; O, 35·53%. The free acid and its *calcium* and *silver* salts are soluble in water. It is readily decomposed by alkalis and reduces ferric salts or iodic acid. The acid contains a pyrrole group which reacts with diazo-salts in much the same manner as pyrrole itself, but quite differently from hemipyrrole.

The pyrrole group, when exposed to the air, in an acidified alcoholic solution, polymerises, and the product gives an absorption band identical with that observed in the spectrum of polymerised pyrrole. When heated with hydrochloric acid, urochrome is decomposed, yielding a *black pigment*: C, 59·16; H, 4·91; N, 9·69; S, 3·55; O, 22·69%.

The normal amount of urochrome eliminated by the human organism in twenty-four hours varies between 0·4 and 0·7 gram, but in cases of infectious diseases, such as typhoid fever, increases considerably.

J. J. S.

Nucleic Acid from the Pancreas (Guanylic Acid). Otto von Fürth and Ernst Jerusalem (*Beitr. chem. Physiol. Path.*, 1907, **10**, 174—187).—Bang states that guanylic acid, the nucleic acid obtained from the pancreas, differs from other nucleic acids, inasmuch as it yields a derivative of glycero-phosphoric acid, yields one-third of its weight on hydrolysis in the form of a reducing sugar, and contains only one basic substance, guanine. All these assertions are now alleged to be incorrect, and there is no necessity to distinguish between guanylic and other nucleic acids of animal origin. W. D. H.

Gelatin Forms Produced by Precipitates of Salts and Crystals. Raphael E. Liesegang (*Chem. Zentr.*, 1907, ii, 415; from *Zeitsch. Chem. Ind. Kolloide*, 1, 364—367. Compare this vol., ii, 337).—The formation of a precipitate, or of crystals of salt or water, may induce gelatin to take certain forms or shapes which are retained after the cause has been removed. Experiments on the crystallisation of potassium dichromate have shown that, contrary to Molisch's theory (*Unters. über das Erfrieren der Pflanzen, Jena*, 1897), the gelatin accumulates at the places where the crystals form. Experiments on freezing gelatin films which had been dyed with methylene-blue proved, however, that both accumulation and dispersion of the gelatin may be caused by the formation of crystals even in the same preparation. E. W. W.

The Amounts of Cystin in Various Horny Materials. Hans Buchtala (*Zeitsch. physiol. Chem.*, 1907, **52**, 474—481. Compare Mörner, Abstr., 1900, i, 128; 1902, i, 331).—The following percentages of cystine have been obtained from the materials mentioned: human hair, 13—14·5; human nails, 5·15; horse hair, 7·98; horses' hoofs, 3·20; ox hair, 7·27; hoofs of oxen, 5·37; pigs' bristles, 7·22; pigs' hoofs, 2·17. J. J. S.

Nitrochitins. OTTO VON FÜRTH and EMIL SCHOLL (*Beitr. chem. Physiol. Path.*, 1907, 10, 188—198).—Chitin is attacked by warm or cold fuming nitric acid alone, or in the presence of sulphuric acid, yielding a mixture of nitrates corresponding in properties with the nitrocelluloses. The chitin dissolves in the acid, and the nitro-products are precipitated by pouring the solution into water. Two products are formed, one of which is insoluble in all the ordinary organic solvents, whereas the other dissolves readily in alcohol, acetone, ethyl acetate, and glacial acetic acid. They are true nitrates, as when hydrolysed with acids or alkalis they yield nitric acid.

Chitosan reacts with nitrous acid, yielding a product with reducing properties soluble in water, acids, and alkalis, but precipitated by alcohol. J. J. S.

Diamino-acids from Koilin. ERICH VON KNAFFL-LENZ (*Zeitsch. physiol. Chem.*, 1907, 52, 472—473).—The following diamino-acids have been obtained by hydrolysing koilin (compare this vol., i, 884) with sulphuric acid: histidine 0·034, arginine 3·596, lysine 1·640. The numbers are parts per 100 of air-dried and ash-free koilin.

J. J. S.

A New Solvent for Some Proteins. IWAN OSTROMYSSLENSKY (*J. pr. Chem.*, 1907, [ii], 76, 267—268).—As Fischer has shown that proteins are complicated amides, it was to be expected (this vol., ii, 847) that they would prove to be soluble in simple amides. It is found that the albumoses and peptones dissolve in formamide and fused acetamide. The latter dissolves over 30% of the peptone of egg-albumin, whereas the albumins, such as egg- and serum-albumins, do not dissolve in this solvent. The concentrated solutions in formamide are viscid at the ordinary temperature, gradually become reddish-brown, and can be filtered. The solubility in formamide may be used in the separation of proteins from each other and from inorganic material. The solutions in acetamide are suitable for use in cryoscopic investigations. G. Y.

Hydrolysis of the Albumoses Occurring in Meat Extract. KARL MICKO (*Zeitsch. Nahr. Genussm.*, 1907, 14, 253—298).—The experiments described were undertaken for the purpose of ascertaining the origin of the amino-acids obtained in the hydrolysis of meat extract (Abstr., 1906, i, 778). The portion of meat extract precipitated by zinc or ammonium sulphate is not identical with either gelatin or gelatoses, and unaltered gelatin cannot be detected in true meat extract itself. During the manufacture of meat extract, gelatin may pass into solution, but it is converted by the lactic acid present into gelatoses or acid glutin. The greater part of the portion precipitated by ammonium sulphate consists of a mixture of proteins having the general properties of albumoses and showing no indications of having been derived from gelatin. A small proportion of these albumoses, however, gives reactions very similar to those obtained with gelatoses, &c. Hydrolysis of the constituents of meat extract which are soluble in saturated ammonium sulphate solution yields monoamino-acids.

W. P. S.

Coaguloses. D. LAWROFF (*Zeitsch. physiol. Chem.*, 1907, 53, 1—7).—In the peptic digestion of proteins, as well as in their digestion by dilute mineral acids, at least two types of coagulose-yielding substances are recognisable. The first are of the type of proteoses, and the coaguloses which arise from them yield on hydrolysis monoamino-acids and basic nitrogenous cleavage products. The second type of coagulose-yielding substances are of the type of polypeptides, and the coaguloses which arise from them yield on hydrolysis only mono-amino-acids. W. D. H.

Racemic Tryptophan. RUDOLF A. ALLERS (*Biochem. Zeitsch.*, 1907, 6, 272—275).—Racemic tryptophan, prepared according to Neuberg's method, and the synthetic preparation of Ellinger and Flamand (this vol., i, 737) both begin to melt at 256°. Optically active tryptophan is stated to melt at 273° by Hopkins and Cole and by Neuberg and Popowsky; at 289° by Abderhalden and Kempe. Racemisation is probably due to the ammonia added at 60° in the process of preparation (compare following abstract). G. B.

Tryptophan. CARL NEUBERG (*Biochem. Zeitsch.*, 1907, 6, 276—282).—An iodine solution, when added to tryptophan dissolved in alkali hydroxide, produces a pale brown, amorphous precipitate having the composition of a mixture of mono- and di-iodotryptophan (compare Neuberg and Popowsky, this vol., i, 253; Nürnberg, this vol., i, 805).

Silver nitrate added to tryptophan dissolved in slightly less than 1 mol. of sodium hydroxide produces a silver salt, $C_{11}H_{11}O_2N_2Ag$.

Tryptophan is racemised by concentrated hydrochloric acid at 170°, and then melts at 254—255°. An optically inactive specimen was also obtained by Neuberg's method of preparation, which involves boiling with lead carbonate and ammonia (compare preceding abstract). G. B.

The Non-existence of Protagon as a Definite Chemical Compound. OTTO ROSENHEIM and M. CHRISTINE TEBB (*J. Physiol.*, 1907, 36, 1—16).—Liebreich's, Gamgee and Blankenhorn's, and Cramer's protagons represent the same substance as cérébrote prepared by Couerbe in 1834. A similar substance is obtained by extracting brain with boiling acetone after the cholesterol has been removed by cold acetone. All these substances may be split into substances of widely varying phosphorus and nitrogen percentage by simple fractional crystallisation at different temperatures, or with different solvents. They also show great difference in optical activity and in the amount of galactose split off by acid hydrolysis. The base sphingosine as well as choline is found amongst the products of protagon hydrolysis. Protagon is not a definite chemical compound, but a mixture of substances, some of which (such as phrenosin) are phosphorus-free and others (such as sphingomyelin) rich in phosphorus. W. D. H.

Protagon. WILLIAM J. GIES (*J. Biol. Chem.*, 1907, 3, 339—358).—The non-identity of protagon as a chemical individual is maintained, and Cramer's attempt to rehabilitate it (see preceding abstract) is shown to rest on obviously fallacious reasoning. W. D. H.

Effect of Colouring Matters on some of the Digestive Enzymes. H. W. HOUGHTON (*J. Amer. Chem. Soc.*, 1907, **29**, 1351—1357).—A study of the effect of various colouring matters on the activity of pepsin has led to the following conclusions. Annatto does not affect the activity of the enzyme towards fibrin, but when present in certain proportions diminishes the activity towards egg-albumin and casein. Saffron lessens the activity towards fibrin, casein, and egg-albumin when it is used in the proportion of 1 : 400, but smaller quantities have no effect. Turmeric reduces the activity towards casein and egg-albumin, but, when present in as small a proportion as 1 : 800, does not affect the digestion of fibrin. Cochineal and Bismarck-brown, when used in a smaller proportion than 1 : 400, do not decrease the activity of the enzyme towards fibrin, but a proportion of 1 : 1600 lessens the activity towards egg-albumin. Crocein-scarlet 1B (1 : 1600) inhibits entirely the action of the enzyme on fibrin, and, when present in the proportion of 1 : 200, it diminishes the activity towards casein and egg-albumin.

Annatto and oil-yellow are found to assist the hydrolysis of butter-fat by lipase, and it is therefore assumed that these colouring matters contain some lipolytically active substance. E. G.

Behaviour of Hippuric Acid to Erepsin. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1907, **52**, 526. Compare Abstr., 1906, ii, 294).—Hippuric acid dissolved in sodium hydrogen carbonate solution is not hydrolysed by erepsin. J. J. S.

Action of the Proteolytic Ferment of Bacillus pyocyaneus. EMIL ZAK (*Beitr. chem. Physiol. Path.*, 1907, **10**, 287—298).—The ferment not only cleaves proteoses into simpler products, but evidence is adduced that it also has a synthetic action both in bouillon cultures and in the filtrate freed from organisms. Taylor (this vol., i, 665) has described previously a reversible action in the case of trypsin.

W. D. H.

Organic Chemistry.

Synthetical Production of Optically Active Petroleum from Glycerides. Julius Lewkowitsch [and Hans Pick] (*Ber.*, 1907, 40, 4161—4162).—Distillation of chaulmoogra oil with zinc dust leads to the formation of gaseous products and a crude petroleum which has the characteristic odour of the higher fractions of the natural oils, and in addition is dextrorotatory. The conclusion is drawn that optically active glycerides, the activity of which is due to the configuration of the fatty acid, yield optically active hydrocarbons (compare C. Neuberg, this vol., i, 577). W. R.

Synthesis of Optically Active Petroleum. Carl Neuberg (*Ber.*, 1907, 40, 4477—4478).—A claim for priority as against Lewkowitsch and Pick (preceding abstract). G. Y.

Dimagnesium Compounds of $\alpha\epsilon$-Dibromopentane. Julius von Braun (*Ber.*, 1907, 40, 4065—4066).—The author claims a prior right to the study of the action of the Grignard reagent on $\alpha\epsilon$-dibromopentane (Braun and Steindorff, Abstr., 1905, i, 341; Grignard and Vignon, this vol., i, 689). C. S.

Behaviour of Various Aldehydes, Ketones, and Alcohols towards Oxidising Agents. Willey Denis (*Amer. Chem. J.*, 1907, 38, 561—594).—Evans (Abstr., 1906, i, 269) has shown that the oxidation of benzoylcarbinol takes place in definite stages in accordance with the scheme put forward by Nef (Abstr., 1905, i, 7). A study has now been made of the oxidation of ethyl alcohol, ethyl ether, acetaldehyde, and acetic acid under various conditions.

When cold aqueous solutions of ethyl alcohol, ether, and acetaldehyde are treated with *N* potassium permanganate, acetic acid only is produced. In presence of excess of potassium hydroxide, however, acetic acid is the main product, but carbonic and oxalic acids also are formed in quantities varying with the strength of the alkali. In all these cases, the first product of the oxidation is acetaldehyde, which in presence of alkali hydroxide of greater concentration than 0·1% (compare McLeod, this vol., i, 172) is partially converted into vinyl alcohol, $\colon C(OH)\cdot CH_2\cdot H \longrightarrow OH\cdot CH\colon CH_2$. In presence of the permanganate, the vinyl alcohol is oxidised to glycollaldehyde, which suffers dissociation, thus: (*a*) $OH\cdot CH_2\cdot CHO \rightleftarrows \colon CH\cdot OH + CH_2O$ and (*b*) $OH\cdot CH_2\cdot CHO \rightleftarrows \colon CH\cdot CHO + H_2O$. The portion dissociated in accordance with (*a*) is converted into carbonic acid with intermediate formation of formic acid, and that dissociated in accordance with (*b*) is converted into glyoxal with oxalic acid as the final product.

When acetone is oxidised in neutral or acid solution, molecular proportions of acetic and carbonic acids are produced, and it is evident therefore that aqueous solutions of acetone do not contain any of the compound in the enolic form. On the addition of potassium hydroxide, however, the presence of *iso*acetone can be proved (1) by its quantitative conversion into mercuric *iso*acetone; (2) by its conversion into diacetone alcohol, and (3) by its oxidation to carbonic and oxalic acids with intermediate formation of acetol.

When acetic acid is treated with alkali hydroxide, it is evident that *iso*acetic acid is not formed, since such a substance would undergo oxidation to oxalic acid with intermediate formation of orthoglycollic acid, $OH\cdot CH_2\cdot C(OH)_3$.

Acetol, in absence of alkali hydroxide, is oxidised to acetic and carbonic acids, whilst, in presence of alkali, it is converted into oxalic and carbonic acids. Experiments have been made which show that pyruvic, hydroxypyruvic, and mesoxalic acids are successive intermediate products of the oxidation of acetol in presence of alkali. Observations have also been made with reference to the oxidation of lactic acid. When acetol is treated with silver oxide, either alone or in presence of potassium hydroxide, molecular quantities of acetic and formic acids are produced, whence it is concluded that only those molecules of acetol are oxidised which are dissociated, thus:

$$CH_3\cdot CO\cdot CH_2\cdot OH \rightleftarrows CH_3\cdot CHO + \colon CH\cdot OH$$

and $CH_3\cdot C(OH)\colon CH\cdot OH \rightleftarrows CH_3\cdot C(OH)\colon + \colon CH\cdot OH$. With mercuric oxide, however, acetol is not oxidised in neutral solution, but, on addition of alkali hydroxide, *r*-lactic acid is produced together with small quantities of formic and acetic acids. In this case, therefore, only those molecules undergo oxidation which are dissociated as follows: $CH_3\cdot CO\cdot CH_2\cdot OH \rightleftarrows CH_3\cdot CO\cdot CH\colon + H_2O$ and

$$CH_3\cdot C(OH)\colon CH(OH) \rightleftarrows CH_3\cdot C(OH)\colon C\colon + H_2O,$$

whence it is evident that pyruvaldehyde is the primary oxidation product and undergoes rearrangement into *r*-lactic acid.

When a concentrated aqueous solution of mesoxalic acid is heated at 100°, the acid is converted quantitatively into glyoxylic and carbonic acids. If the acid is heated at 150° with concentrated potassium hydroxide, theoretical quantities of formic and oxalic acids are produced.

Ethyl diketobutyrate is rapidly converted by solutions of sodium carbonate or hydroxide into methyltartronic acid. When a concentrated solution of methyltartronic acid is heated at 100°, it is decomposed into carbonic and *r*-lactic acids. On heating ethyl diketobutyrate with water at 63—65°, carbon dioxide is slowly evolved and pyruvaldehyde and lactic and oxalic acids are formed. The lactic acid is produced by a rearrangement of the pyruvaldehyde, the latter being formed, thus: $CH_3\cdot CO\cdot CO\cdot CO_2Et + H_2O \longrightarrow CH_3\cdot CO\cdot CO\cdot CO_2H + EtOH \longrightarrow CH_3\cdot CO\cdot CHO + CO_2 + EtOH + H_2O$. When ethyl diketobutyrate is treated with water and silver oxide, molecular quantities of acetic and oxalic acids are obtained. In presence of sodium hydroxide, methyltartronic, oxalic, and acetic acids are produced together with small quantities of carbonic and formic acids. E. G.

Preparation of Monochlorohydrin. Deutsche Sprengstoff Aktien-Gesellschaft (D.R.-P. 180668).—Glycerol (100 parts) is mixed with 150 parts of hydrochloric acid (sp. gr. 1·180 to 1·190) and the mixture heated in an autoclave for fifteen hours at 120° under a pressure of one atmosphere. The mixture, on fractionation under 12—15 mm. pressure, yields first water and excess of acid, then monochlorohydrin at 130—150°, and, finally, the unchanged glycerol at 165—180°. The yield of monochlorohydrin is about 75%, and in these conditions there is no tendency for the formation of the dichlorohydrin. G. T. M.

ψ-Butylene Chlorohydrin, OH·CHMe·CHMe·Cl. K. Krassusky (*Compt. rend.*, 1907, **145**, 762—763).—The ψ-butylene chlorohydrin described by Henry (this vol., i, 887) was obtained by the author in 1902 (Abstr., 1902, i, 425). It can be obtained by addition of hydrochlorous acid to ψ-butylene, prepared either by the action of alcoholic potash on *sec.*-butyl iodide or by withdrawal of bromine from butylene bromide, CHMeBr·CHMeBr, by means of zinc dust in aqueous alcoholic solution. ψ-Butylene chlorohydrin, when heated in a sealed tube with aniline, gives methyl ethyl ketone. By prolonged shaking of the chlorohydrin with lead oxide and water, *s*-dimethylethylene oxide is formed, but by heating with lead oxide and water in a sealed tube at 140° methyl ethyl ketone is produced. When prepared according to the first method, the chlorohydrin contains a small quantity of the *n*-butylene chlorohydrin, revealed in the reaction with lead oxide by production of a small quantity of aldehyde. E. H.

By-products of the Hydrolysis of Tetramethylethylene [βγ-Dimethyl-Δ^{β}-butylene] Bromohydrin. Maurice Delacre (*Bull. Soc. chim.*, 1907, [iv], 1, 978—987. Compare this vol., i, 578). —When βγ-dimethyl-Δ^{β}-butylene bromohydrin is hydrolysed by aqueous potassium hydroxide, the chief product is the hydrocarbon, βγ-dimethyl-Δ^{β}-butylene. The residue contains no appreciable quantity of alcohol, but probably consists of a mixture of isomeric bromides. The latter consist of (1) the bromide of a primary alcohol, not attacked by silver acetate, but forming an acetin when heated at 200° with potassium acetate, probably of the constitution $CHMe_2·CHMe·CH_2Br$, and (2) a bromide which, when treated with silver acetate, gives a tertiary alcohol. No asymmetric compounds were identified, possibly owing to the ease with which the change, $CMe_3·CHMeBr \rightarrow CHMe_2·CMe_2Br$, would be effected. E. H.

Facts and Hypotheses concerning Isomeric Changes in Derivatives of Pinacone. Maurice Delacre (*Bull. Soc. chim.*, 1907, [iv], 1, 987—995. Compare preceding abstract).—Chiefly theoretical. By saturating crude βγ-dimethyl-Δ^{α}-butylene with hydrogen bromide, and acting on the bromide formed with potassium acetate at 200°, a large proportion of an acetin, b. p. 155° (approx.), is formed, which, on hydrolysis, gives an alcohol, b. p. 141°, but is probably different from the acetin boiling at the same temperature obtained by similar treatment of βγ-dimethyl-Δ^{β}-butylene. Whilst βγ-dimethyl-Δ^{β}-butylene readily combines with the haloid acids, βγ-dimethyl-Δ^{α}-butylene does not do so in the cold, and, in order to transform it completely into the chlorohydrin, the hydrocarbon must be heated at 100° with hydrochloric acid for fifteen days. The same chlorohydrin is formed in each case. E. H.

Dimethylketol. I. OTTO DIELS and ERICH STEPHAN (*Ber.*, 1907, 40, 4336—4340).—Pechmann has already described the preparation of dimethylketol, OH·CHMe·COMe, by the reduction of diacetyl. The authors describe a convenient method of preparing diacetyl.

von Pechmann and Dahl (Abstr., 1890, i, 1234) have described two solid modifications of dimethylketol, one with m. p. 126—128°, and the other with m. p. 94—98°. The authors are unable to confirm this, but find that two modifications, with the melting points 95·5° and 85·5° respectively, exist. These modifications are very similar in appearance; they can be crystallised without difficulty, and are dimolecular forms of dimethylketol. The difference between the results obtained by the authors and those obtained by von Pechmann and Dahl is ascribed to the latter authors having used ether in crystallising their compounds; it is found that the polymerides in question cannot be crystallised when ether is present.

Dimethylketol, obtained by the reduction of diacetyl with zinc and dilute sulphuric acid, was allowed to remain in a closed vessel for three and a-half months, when it was transformed into a crystalline *compound*, $C_8H_{16}O_4$, with m. p. 95·5°; that it is a dimolecular form of dimethylketol was shown by a determination of its molecular weight in acetone by the ebullioscopic method.

When a little granulated zinc was added to dimethylketol and the whole immersed in a freezing mixture, the *compound*, $C_8H_{16}O_4$, separated as a crystalline mass, m. p. 85·5°.

Each of these modifications crystallises in rhombic leaflets; their solubilities are of the same order. That they are distinct is shown by the depression of the melting point, which occurs with a mixture of the two.

The *benzoyl* derivative, $C_{11}H_{12}O_3$, obtained by benzoylating dimethylketol in pyridine solution, has b. p. 140—141°/8 mm. and D^{18} 1·104.

A. McK.

Chloromethyl Sulphate. JOSEF HOUBEN and HANS R. ARNOLD (*Ber.*, 1907, 40, 4306—4310).—Chloromethyl ether, prepared from hydrogen chloride and a paste of trioxymethylene and methyl alcohol at 0° (compare Litterschied, Abstr., 1904, i, 962), reacts with sulphur trioxide in a freezing mixture to form *chloromethyl sulphate*, $CH_2Cl·SO_4Me$, b. p. 92°/18 mm., D^{18} 1·473, which is extraordinarily reactive, and is decomposed by water, forming methylsulphuric acid, formaldehyde, and hydrogen chloride.

s-Dichloromethyl ether reacts with sulphur trioxide to form a liquid, b. p. 79°/18—19 mm., which reacts explosively with water, alcohol, acetone, acetic acid, benzene, or light petroleum; the analytical data do not correspond with the formula $(CH_2Cl)_2SO_4$.

C. S.

The Alkaline Hydrolysis of Alkyl Nitrates; a Contribution to the Constitution of Nitric Acid. PETER KLASON and TOR CARLSON (*Ber.*, 1907, 40, 4183—4191. Compare Abstr., 1906, i, 787).—The presence of phenyl hydrosulphide during the hydrolysis of alkyl nitrates prevents the formation of resin; in the absence of hydrosulphide, the peroxide formed is converted into aldehyde, and this gives rise to the resin. With glyceryl trinitrate, the reaction is normal, but with the nitrates derived from monohydric alcohols in addition the hydrosulphide is alkylated. It might be assumed that during the change the nitrate was first reduced to nitrite, the hydrosulphide being oxidised to disulphide, and then that hydrolysis of the nitrite occurred, so that a quantitative examination was necessary to decide between (I) $R{\cdot}NO_3 + KSR^1 = R{\cdot}S{\cdot}R^1 + KNO_3$ and (II*a*) $R{\cdot}NO_3 + KSR^1 + HSR^1 = R{\cdot}NO_2 + KOH + R^1S{\cdot}SR^1$, (*b*) $R{\cdot}NO_2 + KOH = KNO_2 + R{\cdot}OH$.

It was found that the velocity of hydrolysis with sodium phenylsulphide was 100 to 200 times that with alkali alone. The first step was the determination of χ, the ratio of $x : y$, where x and y are the decrease in the concentration of nitrate due to reactions I and II*a*. The value of χ was found to be independent of the time, and consequently the two reactions proceed simultaneously.

By determining the concentration of the alkali, it was found that the hydrolysis is a reaction of the second order in both cases, and the constant obtained is the sum of those due to the two reactions. The proportion of nitrate hydrolysis, k_x, to nitrite hydrolysis, k_y, for various alkyl nitrates is appended:

	K_x.	K_y.
Ethyl nitrate	0·0243	0·0082
n-Propyl nitrate	0·0160	0·0082
*iso*Butyl nitrate............	0·0013	0·0078
*iso*Amyl nitrate	0·0081	0·0083

With methyl nitrate, the hydrolysis to nitrate and phenyl methyl sulphide is almost quantitative, only 0·7% of nitrite being formed. The velocity of nitrate hydrolysis decreases rapidly as the series is ascended, and that of nitrite is practically constant. W. R.

The Alkaline Hydrolysis of Alkyl Nitrates in the Presence of Hydrogen Peroxide. TOR CARLSON (*Ber.*, 1907, **40**, 4191—4194. Compare preceding abstract).—In the hydrolysis of alkyl nitrates, the proportion of nitrate and nitrite may be determined by evaporation of the solvent and unchanged alkyl nitrate in a vacuum, the residue being treated with potassium iodide and hydrochloric acid, and the nitric acid decomposed by iron chloride. The values obtained at 70° with 95% alcohol, concentration 0·5*N*, are: CH_3NO_3, nitrite, trace; $EtNO_3$, 7% nitrite; $Pr^{\alpha}NO_3$, 17% nitrite; i-$BuNO_3$, 35% nitrite; i-$C_5H_{11}NO_3$, 20% nitrite. The results are not particularly accurate in consequence of the reducing action of aldehyde. With nitrates of polyatomic alcohols, the reaction velocity is greater and more nitrite is formed; glyceryl trinitrate giving 67%, glycyl dinitrate 87%, and nitrocellulose (12·5% N) 82%. In these reactions, the alkyl complex is destroyed and glycol, glycerol, and cellulose are not regenerated.

Now if peroxide is formed during hydrolysis, oxygen should be liberated when hydrogen peroxide is present, $R{\cdot}CH_2O{\cdot}OH + HO{\cdot}OH = R{\cdot}CH_2{\cdot}OH + H_2O + O_2$, and this is proved to be the case; nitrocellulose, evolving oxygen and hydrated cellulose, being generated. Experiments should give according to theory 1 mol. of O_2 for every mol. of nitrite;

this is not realised, due, perhaps, to catalytic decomposition of peroxide by alkali, and also the alcohol behaving as an "acceptor."

Benzyl nitrate and alkali phenyl sulphide give almost no nitrite, but phenyl benzyl sulphide and nitrate. W. R.

Relative Volatility of Various Groups of Acetic Esters. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 742—764).—This paper is supplementary to two already published (Abstr., 1903, ii, 8; this vol., i, 674). The replacement of a hydrogen atom by an acetyl group should lower the volatility in proportion to the increase in molecular weight, but this effect is liable to be obscured by other influences. For example, (1) the position of the hydrogen atom substituted; (2) when the hydrogen atom is attached to a carbon atom, the nature of the other groups or elements connected with the latter, and (3) the relative extents to which the molecules of the parent substance and of its acetyl derivative are associated. The coefficients of association have different values, not only for compounds possessing different chemical functions, but also for substances of the same function but containing different numbers of carbon atoms in the molecule.

A large number of tables are given in the original, showing the volatility relations between substances of the same types and their acetyl derivatives, and exemplifying the effects of the several influences, and especially of the third, referred to above. The following examples may be quoted. Ethyl acetate boils 1° below ethyl alcohol, whilst difluoroethyl acetate boils 11° higher than the corresponding alcohol. The reason of this difference is found in Swarts' observation (Abstr., 1903, i, 222) that difluoroethyl alcohol is much less associated than ethyl alcohol. Similarly, the effect of a lower association value is shown by the replacement of hydrogen by acetyl in the SH group of ethyl mercaptan, which leads to an increase of 80° in the boiling point, whereas the analogous substitution in the case of ethyl alcohol lowers the boiling point by 1°. T. A. H.

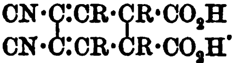
[Preparation of Salts of the Iodated Higher Fatty Acids.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 180622).—*Calcium iodobehenate*, $Ca(C_{22}H_{42}O_2I)_2$, is most conveniently prepared in a stable condition by slowly adding an alcoholic solution of behenic acid to the filtered solution produced by dissolving hydrated calcium chloride in alcohol and precipitating ammonium chloride by passing in an excess of ammonia. The organic calcium salt separates as a colourless powder, insoluble in water or alcohol. This compound may also be prepared either by double decomposition from an alkali iodobehenate and calcium chloride or by mixing equivalent amounts of the acid and calcium hydroxide dissolved in water. *Strontium* and *magnesium iodobehenates*, *calcium* and *strontium iodostearates*, and *calcium iodopalmitate* were also prepared by the foregoing methods, and similarly obtained as colourless, insoluble powders.

G. T. M.

Preparation of Iodobehenic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186214).—Although the chlorine in chlorobehenic acid is not replaced by iodine on treating this substance with metallic iodides, nevertheless the corresponding bromo-compound readily undergoes this substitution. Bromobehenic acid, obtained by adding hydrogen bromide to erucic acid, when warmed with sodium iodide and glacial acetic acid furnishes iodobehenic acid. Other metallic iodides may be employed instead of sodium iodide, and the solvent or diluent may also be varied. G. T. M.

Preparation of Bromo-Aliphatic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186740).—It has been found that the unsaturated aliphatic acids readily combine with nascent hydrogen bromide, and become thus converted into bromo-aliphatic acids. A mixture of erucic acid, potassium bromide, and concentrated sulphuric and glacial acetic acids when shaken at a high temperature give rise to bromobehenic acid. Bromostearic acid was obtained by warming and shaking a mixture of oleic acid, sodium bromide, and an acetic acid solution of hydrogen chloride. G. T. M.

Mono- and Di-alkylcyanovinylacetic [Mono- and Di-alkyl-cyano-Δ^{β}-butenoic] Acids. II. ICILIO GUARESCHI (*Mem. Accad. Sci. Torino*, 1907, [ii], 57, 287—307. Compare Abstr., 1901, i, 630). —The author has prepared a number of substituted β-butenoic acids of the types: (1) $CN\cdot CH{:}CR\cdot CH_2\cdot CO_2H$; (2) $CN\cdot CH{:}CR\cdot CHR\cdot CO_2H$; (3) $CN\cdot CH{:}CR\cdot CHR'\cdot CO_2H$, and (4) $CN\cdot CH{:}CR'\cdot CHR\cdot CO_2H$, R representing an alkyl and R′ an aromatic radicle. These acids are energetic reducing agents, absorb bromine, and give colorations with alkali or, better, ammonium carbonate, or with potassium nitrite. When they are stored in glass vessels, the latter become coloured, owing to the alkalinity of the glass. With ferric chloride, acids of type (1) give a coloration, whilst those of types (2), (3) and (4) undergo condensation, yielding hexa-substituted derivatives of dihydrophthalic acid of the form:



$$\begin{array}{l} CN\cdot C{:}CR\cdot CR\cdot CO_2H \\ CN\cdot C{:}CR\cdot CR\cdot CO_2H \end{array}.$$

The above Δ^{β}-butenoic acids are prepared by the action of 60% sulphuric acid on (1) 3 : 5-dicyano-2 : 6-diketo-4-alkyl-Δ^3-tetrahydropyridines, which are converted, by way of unstable tricarboxylic acids, into γ-cyano-β-alkyl-Δ^{β}-butenoic acids; (2) 3-cyano-2 : 6-diketo-4-alkyl-Δ^3-tetrahydropyridines or 3-cyano-2 : 6-diketo-4 : 5-dialkyl-Δ^3-tetrahydropyridines; in no case was the intermediate di- or tri-carboxylic acid isolated.

γ-Cyano-$\alpha\beta$-dimethyl-Δ^{β}-butenoic acid, $CN\cdot CH{:}CMe\cdot CHMe\cdot CO_2H$, prepared from 3-cyano-2 : 6-diketo-4 : 5-dimethyl-Δ^3-tetrahydropyridine, crystallises from water in colourless or faintly yellow, acicular prisms, m.p. 191·5—192°, forms a yellowish-brown *copper* salt, $(C_7H_8O_2N)_2Cu$, rapidly reduces potassium permanganate or auric chloride, but does not reduce Fehling's solution.

γ-Cyano-β-methyl-α-ethyl-Δ^{β}-butenoic acid,

$$CN\cdot CH{:}CMe\cdot CHEt\cdot CO_2H,$$

prepared from 3-cyano-2 : 6-diketo-4-methyl-5-ethyl-Δ^3-tetrahydropyridine, crystallises from water in colourless, prismatic needles or short prisms, m. p. 175—176°.

γ-Cyano-α-methyl-β-ethyl-Δ^β*-butenoic acid*,

$$CN\cdot CH{:}CEt\cdot CHMe\cdot CO_2H,$$

prepared from 3-cyano-2 : 6-diketo-5-methyl-4-ethyl-Δ^3-tetrahydropyridine, has m. p. about 200°.

γ-Cyano-β-propyl-Δ^β*-butenoic acid*, $CN\cdot CH{:}CPr^\alpha\cdot CH_2\cdot CO_2H$, prepared from 3 : 5-dicyano-2 : 6-diketo-4-propyl-Δ^3-tetrahydropyridine, or the ammonium derivative of its enolic form, crystallises from alcohol in prisms or needles, m. p. 225—227° (decomp.).

*γ-Cyano-β-*iso*propyl-*Δ^β*-butenoic acid*, $CN\cdot CH{:}CPr^\beta\cdot CH_2\cdot CO_2H$, prepared from 3 : 5-dicyano-2 : 6-diketo-4-*iso*propyl-Δ^3-tetrahydropyridine, forms crystals, m. p. 177—178°.

γ-Cyano-β-methyl-α-propyl-Δ^β*-butenoic acid*,

$$CN\cdot CH{:}CMe\cdot CHPr\cdot CO_2H,$$

prepared from 3-cyano-2 : 6-diketo-4-methyl-5-propyl-Δ^3-tetrahydropyridine, crystallises from water in colourless or faintly yellow, acicular prisms, m. p. 154—155°, and forms a crystalline *dibromide*, $C_9H_{13}O_2NBr_2$.

γ-Cyano-β-hexyl-Δ^β*-butenoic acid*, $CN\cdot CH{:}C(C_6H_{13})\cdot CH_2\cdot CO_2H$, prepared from 3 : 5-dicyano-2 : 6-diketo-4-hexyl-Δ^3-tetrahydropyridine, has m. p. 175—180°.

γ-Cyano-β-phenyl-Δ^β*-butenoic acid*, $CN\cdot CH{:}CPh\cdot CH_2\cdot CO_2H$, prepared from 3-cyano-2 : 6-diketo-4-phenyl-Δ^3-tetrahydropyridine or from the ammonium salt of 3 : 5-dicyano-2 : 6-diketo-4-phenyl-Δ^3-tetrahydropyridine, crystallises from alcohol in colourless or faintly yellow plates, m. p. 256—257°.

*γ-Cyano-β-*m*-tolyl-*Δ^β*-butenoic acid*, $CN\cdot CH{:}C(C_6H_4Me)\cdot CH_2\cdot CO_2H$, prepared from the ammonium salt of 3 : 5-dicyano-2 : 6-diketo-4-*m*-tolyl-Δ^3-tetrahydropyridine, crystallises from acetic acid in short, heavy, colourless or faintly yellow prisms, m. p. 255—257°.

γ-Cyano-β-cumyl-Δ^β*-butenoic acid*, $CN\cdot CH{:}C(C_6H_4Pr^\alpha)\cdot CH_2\cdot CO_2H$, prepared from 3 : 5-dicyano-2 : 6-diketo-4-cumyl-Δ^3-tetrahydropyridine, separates from alcohol in crystals, m. p. 240°.

γ-Cyano-α-benzyl-β-methyl-Δ^β*-butenoic acid*,

$$CN\cdot CH{:}CMe\cdot CH(CH_2Ph)\cdot CO_2H,$$

prepared from 3-cyano-2 : 6-diketo-4-methyl-5-benzyl-Δ^3-tetrahydropyridine, forms colourless crystals, m. p. 156—157°.

γ-Cyano-β-ethyl-Δ^β-butenoic, γ-cyano-β-*iso*butyl-Δ^β-butenoic, γ-cyano-α-methyl-β-*iso*propyl-Δ^β-butenoic, and γ-cyano-β-methyl-α-allyl-Δ^β-butenoic acids have also been obtained in small quantities, but have not been analysed. T. H. P.

Complex Salts of Uranium Peroxide. ARRIGO MAZZUCCHELLI and FERRUCCIO BIMBI (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 576—584. Compare this vol., ii, 54).—The following derivatives of uranium peroxide, prepared by the authors, are yellow or orange-yellow in colour, and are decomposed by water with precipitation of uranium peroxide.

$UO_4,UO_2(OAc)_2,2NH_4\cdot OAc$ was obtained by the interaction of uranium nitrate, ammonium acetate, and hydrogen peroxide;

$UO_4,Ba(OAc)_2,6H_2O$, by the interaction of uranyl and barium acetates, acetic acid, and hydrogen peroxide;

$$UO_4,UO_2(C_5H_9O_2)_2,2NaC_5H_9O_2,13H_2O,$$

from uranyl nitrate, sodium valerate, and hydrogen peroxide; the three compounds: (1) $UO_4,UO_2(C_2O_4\cdot NH_4)_2$,

(2) $UO_4,UO_2(C_2O_4\cdot NH_4)_2,2(NH_4)_2C_2O_4,7H_2O$, and

(3) $UO_4,UO_2(C_2O_4\cdot NH_4)_2,2(NH_4)_2C_2O_4,3H_2O$,

from ammonium uranyl oxalate, ammonium oxalate, and hydrogen peroxide; $NaO_2\cdot UO_2\cdot C_8H_4O_4Na,5H_2O$, from sodium uranyl phthalate and hydrogen peroxide. The compound formed by sodium uranyl succinate and hydrogen peroxide is obtained as a yellow precipitate, but was not purified or analysed.

With uranyl nitrate, chloride, sulphate, &c., hydrogen peroxide gives orange-coloured liquids, but the compounds formed could not be isolated. With sodium uranyl pyrophosphate, the *compound* $2UO_4,Na_4P_2O_7,18H_2O$ or $[NaO_2\cdot UO_2\cdot O\cdot PO(ONa)\cdot]_2O$ (?) is obtained, and with ammonium uranyl carbonate the *compound*

$$UO_4,(NH_4)_2CO_3,2H_2O$$

or $NH_4\cdot O_2\cdot UO_2\cdot CO_3\cdot NH_4$. T. H. P.

Complex Salts of Iridium. Irido-oxalates. CESARE GIALDINI (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 551—561).—When a solution of iridic chloride or an alkaline iridichloride is treated with excess of potassium or sodium hydroxide, the principal reaction, represented by: $IrCl_4 + 4KOH = IrO_2 + 4KCl + 2H_2O$, is accompanied by secondary reactions, expressed by the equations: $2IrCl_4 + 7KOH = Ir_2O_3 + 7KCl + 3H_2O + HClO$; $HClO + KOH = KCl + H_2O + O$; $Ir_2O_3,Aq + O = 2IrO_2,Aq$. Hence, in order to prevent the ready decomposition of the hydroxide, $Ir(OH)_4$, it is necessary to limit as far as possible the reaction: $Ir(OH)_4 + Cl' \rightleftarrows Ir(OH)_3 + HClO$. By adding hypochlorous acid, it is found possible to displace the equilibrium of this reaction from right to left, and so facilitate the precipitation of iridium dioxide, the preparation and separation of which usually occupy several days.

The action of oxalic acid on iridium dioxide takes place in two stages: $2IrO_2 + H_2C_2O_4 = Ir_2O_3 + H_2O + 2CO_2$ and $Ir_2O_3 + 6H_2C_2O_4 = 2H_3Ir(C_2O_4)_3 + 3H_2O$, for the completion of which it is necessary to boil the solution for thirty to thirty-five hours. *Potassium sesqui-irido-oxalate*, $K_3Ir(C_2O_4)_3,4H_2O$, prepared by neutralising the acid with potassium carbonate, separates from water in pale orange-yellow, triclinic crystals [Zambonini, $a:b:c = 0.7319:1:0.9565$; $\alpha = 88°34'37''$, $\beta = 94°30'12''$, and $\gamma = 57°1'18''$]. T. H. P.

Oxymethylenecamphor and Mesityloxidoxalic Esters. WILHELM FEDERLIN (*Annalen*, 1907, **356**, 251—280).—Wislicenus's studies of tautomeric compounds (Abstr., 1896, i, 552; 1900, i, 9) led to the conclusion that solvents with slight dissociating powers and non-dissociating solvents favour the formation of the enolic form of desmotropic compounds, whilst the ketonic form is stable in strongly dissociating solvents. This rule, however, does not hold good for all tautomeric substances. Two exceptions, oxymethylenecamphor and mesityloxidoxalic ester, have been studied spectrometrically by Brühl (Abstr., 1899, ii, 735). The present author has investigated the behaviour of the same substances by Wislicenus's ferric chloride colorimetric method (Abstr., 1900, i, 9). The results obtained with oxymethylenecamphor confirm Brühl's statement (*loc. cit.*) that this substance has the ketonic constitution and that enolic transformation does not take place either in feebly or strongly dissociating solvents.

β-Mesityloxidoxalic esters do not give a coloration with ferric chloride in ether, benzene, or chloroform solution, but after some time give a slight coloration in ethyl- or methyl-alcoholic solution. On the other hand, the enolic or α-esters undergo the ketonic transformation rapidly in methyl- or ethyl-alcoholic, but only slowly in ethereal or benzene, and most slowly in chloroform, solution. In these solvents, the β-esters slowly polymerise, the polymerisation being accelerated by exposure of the solution to light. In consequence of preceding ketonic transformation, the α-esters yield the same polymerides in the above solvents with the exception of chloroform. The ketonic transformation of the α-esters and the polymerisation of the β-esters do not take place completely even on prolonged action of the solvent. A converse transformation from the polymeride could not be observed. The propyl and amyl esters polymerise more slowly than do methyl and ethyl mesityloxidoxalates.

The *polymeride* of ethyl mesityloxidoxalate, $(C_{10}H_{14}O_4)_2$, formed in eight days, separates in monoclinic crystals [$a:b:c = 1{\cdot}9825:1:1{\cdot}7810$; $\beta = 143°16'$], m. p. 175°, sublimes unchanged, is less soluble than the β-ester, and does not give a coloration with ferric chloride.

The *polymeride* of methyl mesityloxidoxalate, $(C_9H_{12}O_4)_2$, formed in ten to twelve days, separates in monoclinic crystals [$a:b:c = 1{\cdot}0319:1:1{\cdot}1761$; $\beta = 91°54'$], m. p. 225°, and has properties similar to those of the polymeride of the ethyl ester. A *polymeride*, $(C_9H_{12}O_4)_2$, m. p. 236—237° (partial decomp.), which resembles, but is slightly less stable than, the preceding substance, is obtained when the solid β-methyl ester is exposed to diffused light for eight days.

Propyl mesityloxidoxalate, prepared by the action of sodium on mesityl oxide and propyl oxalate in ethereal solution, is obtained as a yellow oil, b. p. 120—150°/20 mm., which gives a strong coloration with ferric chloride. The *α-ester* forms a green, crystalline *copper* salt, $(C_{11}H_{15}O_4)_2Cu,H_2O$, from which it is liberated by treatment with chloroform and dilute sulphuric acid. The *polymeride*, $(C_{11}H_{16}O_4)_2$, m. p. 111°, forms in ninety days, sublimes with partial decomposition, and does not give a ferric chloride reaction.

Amyl mesityloxidoxalate, prepared from amyl oxalate, is obtained as a yellow oil, b. p. 100—130°/20 mm., gives a strong ferric chloride reaction, and forms a green, crystalline *copper* salt, $(C_{13}H_{19}O_4)_2Cu,H_2O$, which loses H_2O at 115°; m. p. 129—130°. The *α-ester* is obtained from the copper salt as a viscid, yellow oil. The *polymeride*, $(C_{13}H_{20}O_4)_2$, formed in one hundred and twenty days, separates from light petroleum in crystals, m. p. 113—114°. G. Y.

Preparation of Methylenecitryl Halides. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 186659).—Methylenecitric acid is a somewhat unstable substance, which cannot be converted into its chloride or bromide by means of either phosphorus trichloride or tribromide, or the corresponding oxyhalide. It has now been found that this reaction may be readily effected by means of phosphorus pentachloride or pentabromide. Methylenecitric acid (1 part) is mixed with 2 parts of phosphorus pentachloride, hydrogen chloride is evolved, and the oxychloride produced is distilled off, whilst the *methylenecitryl chloride*, $CH_2{<}\genfrac{}{}{0pt}{}{-O-}{CO_2}{>}C(CH_2\cdot COCl)_2$, colourless prisms, m. p. 74—75°, is crystallised from benzene or chloroform with the addition of light petroleum. *Methylenecitryl bromide*, a viscid oil, is obtained when the phosphorus pentachloride is replaced in the foregoing experiment by 4 parts of phosphorus pentabromide. The alkali methylenecitrates may be employed in these reactions in place of the free acid. G. T. M.

Condensation of the Esters of Mesoxalic or Oxalacetic Acid with the Esters of Cyanoacetic Acid. CH. SCHMITT (*Ann. Chim. Phys.*, 1907, [viii], 12, 406—432).—Mainly a résumé of work already published (compare Abstr., 1905, i, 508; 1907, i, 112), but the following compounds are described for the first time. *Methyl αγ-dicyanopropane-αββγ-tetracarboxylate*,

$$C(CO_2Me)_2[CH(CN)\cdot CO_2Me]_2,$$

m. p. 120°, prepared by the action of methyl mesoxalate on excess of methyl cyanoacetate, yields the *compound*, $C_{20}H_{21}O_{11}N_3$, m. p. 115°, on treatment with alcoholic hydrogen chloride; *ββ-dimethyl αγ-diethyl αγ-dicyanopropane-αββγ-tetracarboxylate*, $C(CO_2Me)_2[CH(CN)\cdot CO_2Et]_2$, m. p. 73°, is similarly obtained from methyl mesoxalate and ethyl cyanoacetate; its isomeride, the αγ-dimethyl ββ-diethyl ester,

$$C(CO_2Et)_2[CH(CN)\cdot CO_2Me]_2,$$

already described (Abstr., 1905, i, 508), gives the *compound*,

$$C_{22}H_{23}O_{11}N_3,$$

m. p. 116°, when treated with alcoholic potassium hydroxide.

The esters of mesoxalic acid condense with certain aromatic amines at the ordinary temperature to form derivatives of the type:

$$C(NHR')_2(CO_2R)_2,$$

of which the following are described: *methyl bisanilinomesoxalate*,

$$C(CO_2Me)_2(NHPh)_2,$$

m. p. 113·5°, *ethyl bisanilinomesoxalate*, $C(CO_2Et)_2(NHPh)_2$, m. p. 103°, and *methyl bis-o-toluidinomesoxalate*, $C(CO_2Me)_2(NH\cdot C_7H_7)_2$, m. p. 172°. M. A. W.

Additive Compound of Two Dicarboxyglutaconic Ester Radicles. MAX GUTHZEIT [and ERNST HARTMANN] (*Ber.*, 1907, 40, 4043).—In the course of a study of the halogen derivatives of ethyl dicarboxyglutaconate, a crystalline *compound*, $C_{30}H_{42}O_{16}$, m. p. 86°, has been obtained by heating ethyl bromodicarboxyglutaconate with ethyl sodiodicarboxyglutaconate in xylene solution. This compound, which is formed also in a 90% yield by the action of iodine on ethyl sodiocarboxyglutaconate in toluene solution, or by prolonged boiling of the copper derivative of the ester with finely-divided sulphur in benzene, reacts readily with alcoholic sodium ethoxide in the cold. Its behaviour towards bromine, alkaline permanganate, and tin and glacial acetic acid shows that it does not contain an ethylene linking.

G. Y.

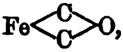
Preparation of Thioglycollic Acid from Chloroacetic Acid. KALLE & Co. (D.R.-P. 180875).—When chloroacetic acid is treated in alkaline solution with sodium sulphide and sulphur, a dithioglycollic acid is produced, and this substance on reduction either with zinc dust or hydrogen sulphide furnishes thioglycollic acid, $HS\cdot CH_2\cdot CO_2H$.

G. T. M.

Deaminocystine and Aminoethyl Disulphide. CARL NEUBERG and ERICH ASCHER (*Biochem. Zeitsch.*, 1907, **5**, 451—455).—By the gentle action of nitrous acid on cystine, *a-hydroxypropionic acid β-disulphide*, $S_2[CH_2\cdot CH(OH)\cdot CO_2H]_2$, can be obtained as the *barium* salt; $[\alpha]_D^{22}$ $-19·08°$. By precipitation of the latter with sulphuric acid, the disulphide is obtained in solution; $[\alpha]_D$ $-10·6°$. On dry distillation, cystine loses carbon dioxide and yields a small quantity of aminoethyl disulphide, $S_2(CH_2\cdot CH_2\cdot NH_2)_2$, which can be isolated as the picrate, m. p. 197°.

G. B.

Conversion of Methyl Alcohol into Formaldehyde and the Preparation of Formalin. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1023—1044. Compare this vol., i, 892).—The experiments were performed either in the apparatus described previously or in a slightly simplified form of it. The following catalysts are very energetic, but produce chiefly carbon dioxide and monoxide, hydrogen and oxygen, the quantity of formaldehyde in the product being very slight: asbestos containing (1) freshly-reduced powdered copper; (2) a mixture of cerium sulphate and thorium oxide; (3) platinum-black. With coke coated with reduced copper, 39·78% of alcohol was changed directly into formaldehyde, whilst, with metallic platinum, 41% was so changed. Contrary to the statement of Sabatier and Senderens, the former substance hardly acts as a catalyst at all, even at 300°, when methyl alcohol is passed over it without admixture of air.

The reaction is exothermic, 31·1 Cal. being evolved for every gram-molecule of methyl alcohol converted into formaldehyde; consequently if the reaction is once started, it should, under certain conditions, proceed without any further application of external energy. A method, which can also be applied technically, has been devised, and 49% of methyl alcohol can thus be transformed when freshly-reduced copper gauze is employed as catalyst; the alcohol must not contain more than 1% of acetone. With platinum or iron filings as catalysts, the yields are unsatisfactory. When methyl alcohol without admixture of air is passed over heated iron filings, the products obtained are carbon monoxide and dioxide, hydrogen, oxygen and methane, carbon, very small quantities of formaldehyde, and a gas, possibly $(CH)_2O$, the constitution of which has not yet been finally determined; with iron it may form  $Fe{<}^{C}_{C}{>}O$, which on heating decomposes forming $Fe+CO+C$.

The percentage composition of the gases depends on the strength of alcohol employed and the rate of passage of the alcohol vapours over the catalyst. Z. K.

Metacetaldehyde. ARTHUR HANTZSCH and J. OECHSLIN (*Ber.*, 1907, **40**, 4341—4344).—Metacetaldehyde has hitherto been considered by the majority of those who have investigated it as stereoisomeric with paracetaldehyde, and accordingly to be a termolecular form of acetaldehyde. The authors are led to the following conclusions. Metacetaldehyde exists in one form only; when pure, it is quite stable; it is not changed when dissolved in phenol, that is, acetaldehyde is not formed. Metacetaldehyde is not termolecular, but is quadrimolecular in phenol solution; in thymol solution, it is probably sexamolecular. From these results, it is certain that metacetaldehyde is not isomeric with paracetaldehyde. A. McK.

Action of Magnesium Hydroxide on Chloral Hydrate. LEOPOLD ROSENTHALER and R. REIS (*Chem. Zentr.*, 1907, ii, 891; from *Apoth. Zeit.*, 1907, **22**, 678—679).—Chloroform is not decomposed when heated with magnesium hydroxide on a water-bath. Chloral hydrate when similarly treated is decomposed chiefly into chloroform and formic acid, but at the same time a secondary reaction takes place whereby a greater proportion of magnesium hydroxide is neutralised, carbon monoxide and magnesium chloride also being formed. The action of magnesium hydroxide on chloral hydrate cannot therefore be employed in the quantitative estimation of the latter compound. W. H. G.

Solubility of Bisulphite Compounds of Aldehydes and Ketones. JOHN B. COPPOCK (*Chem. News*, 1907, **96**, 225).—It has been observed that when aldehydes or ketones are treated with the deep yellow solution prepared by saturating sodium carbonate solution with sulphur dioxide, the bisulphite compounds do not separate. Experiments have been carried out which show that this is due to the solubility of the compounds in sulphurous acid, and it has been found that in preparing the bisulphite solutions from sodium carbonate the sulphur dioxide should only be passed into the solution until a very pale green tint appears. E. G.

Preparation of Formaldehydesulphoxylates. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 180832. Compare Abstr., 1906, i, 400).—Acetone and its homologues react with alkali hyposulphites to form crystallisable ketonesulphoxylates. A dilute aqueous solution of acetone is saturated with sulphur dioxide and the liquid then treated in the cold with zinc dust, the temperature being finally raised to 50—60°. After cooling, the solution deposits zinc acetonesulphoxylate, which is converted into the sodium salt by treatment with sodium carbonate. The sodium acetonesulphoxylate when treated in water with aqueous formaldehyde is readily changed into sodium formaldehydesulphoxylate, whilst the acetone is eliminated. G. T. M.

Combined Sulphurous Acids. II. WILHELM KERP and EMIL BAUR (*Chem. Zentr.*, 1907, ii, 970—971; from *Arb. Kais. Ges.-A.*, 1907, **26**, 231—268. Compare Abstr., 1904, i, 713).—It has been shown that formaldehyde-sulphurous acid and acetaldehyde-sulphurous acid are both strong acids, and it is therefore highly probable that the sulphurous acids of benzaldehyde, acetone, and arabinose are also strong acids. This could not be proved, however, by electrical conductivity measurements, because of the high degree of dissociation of the complex in water. As a rule, the degree of dissociation of the complex is greater in an acid solution than in a neutral solution, from which it follows that the dissociation of the non-ionised acid is greater than that of the anion. The rate of dissociation of the complex is, however, diminished by the presence of an acid.

The addition of acetaldehyde to an aqueous solution of acetaldehyde sodium hydrogen sulphite diminishes the degree of dissociation of the complex in agreement with the law of mass action. The dissociation of the complex increases with a rise of temperature.

Chloral sodium hydrogen sulphite, $CCl_3 \cdot CHO,HSO_3Na$, obtained in a crystalline form by passing sulphur dioxide into a solution of sodium carbonate to which is added a solution of chloral hydrate, is, unlike the latter compound, decomposed to a high degree in aqueous solution.

W. H. G.

The Ammonia Reaction for Distinguishing between Enolic and Ketonic Derivatives. ARTHUR MICHAEL and HAROLD HIBBERT (*Ber.*, 1907, **40**, 4380—4388. Compare Hantzsch and Dollfus, Abstr., 1902, i, 223, 675; Hantzsch, this vol., i, 927).—The authors tested this reaction by inquiring (1) how far the assumption is correct that the reaction $\cdot CH_2 \cdot CO \cdot + NH_3 \longrightarrow \cdot CH_2 \cdot C(OH) \cdot NH_2$ is slower than the salt formation $\cdot CH{:}C(OH) \cdot + NH_3 \longrightarrow \cdot CH{:}C(ONH_4) \cdot$, and, also, if the intramolecular change $\cdot CH_2 \cdot CO \longrightarrow CH{:}C(OH)$ takes place with measureable velocity; (2) if there really exists a sharp difference between the solvents, chloroform, benzene, and toluene, on the one hand, and ether, on the other; (3) whether all real acids and enolic compounds gives instantaneously stable insoluble ammonium salts, as does benzoic acid.

It is found that, in general, enols react more easily than ketones, but there are exceptions, for instance, acetylacetone and the ketonic ethyl diacetoacetate, the former gives the *ammonia* compound, CH_2Ac_2,NH_3, stable at 5°, m. p. 65—67°, at once on mixing a toluene solution with *N*/4 ammonia in toluene, or at − 10° with ether, carbon tetrachloride, or toluene solutions. The reaction velocity does not depend solely on the structure, but also on the "chemical potential" of the interacting compounds.

Triethylamine when mixed with either the ketonic or enolic modification of dibenzoylacetylmethane in acetonitrile or ethyl bromide solution at − 10° gives instantaneously the yellow colour of the salt with the same intensity in either case. Inasmuch as the ketonic isomeride is fairly stable in these media, the conclusion is drawn that the ketonic ⟶ enolic change takes place practically instantaneously.

The authors cannot confirm the alleged difference between ether and other solvents; sometimes precipitation occurs more quickly in toluene solution, sometimes in ether: the speed of precipitation depends, not only on the stability and insolubility of the ammonium salt, but also on the phenomena of supersaturation, as, when experiments are carried out at – 10° with acetylacetone, the additive product is at once precipitated, whereas at – 5° there is a decrease in the velocity with increasing dilution.

The use of benzoic acid (*k* 0·0060) as a typical acid is criticised. When phenylacetic acid (*k* 0·0055) of approximately the same strength as benzoic acid is treated with ammonia in benzene, precipitation of the salt is not instantaneous; 0·0025 of acid in 5 c.c. dry benzene with 4 c.c. *N*/480 ammoniacal benzene takes four minutes at 15° before crystals appear, although the solubility of salt is 1 in 15,000.

In the case of acetic acid, ammonia does not at once produce a precipitate when the acid is in excess, although ammonium acetate is insoluble; this is explained by assuming the formation of a soluble hydrogen salt.

The "ammonia reaction" cannot therefore be used to distinguish between enolic and ketonic compounds.

The additive compounds with phloroglucinol, dimethyldihydroresorcin, and methyldihydroresorcin have m. p.'s 88—91°, 130°, and 137—140° respectively. W. R.

Decomposition of Pentaerythritol Tetraformate on Heating. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 166—168).—The ease with which $\Delta^{\alpha\gamma\epsilon}$-hexatriene is obtained (van Romburgh and van Dorssen, Abstr., 1906, i, 722) by heating *s*-divinylglycol formate has led to a study of the decomposition of the formates of polyhydric alcohols.

Pentaerythritol tetraformate, m. p. 57°, does not decompose in the same manner as *s*-divinylglycol formate, but, on heating at 220—230°, carbon monoxide is evolved and pentaerythritol regenerated. E. G.

Derivatives of the C_5 Sugars from Meta- and Para-Saccharin. HEINRICH KILIÁNI and A. SAUTERMEISTER (*Ber.*, 1907, **40**, 4294—4296. Compare Abstr., 1904, i, 373).—Although meta- and para-saccharinic acids are entirely different in constitution, their barium salts crystallise together, and the quinine salts show almost identical melting points and solubility. The corresponding C sugars obtained on reduction are different, but their oximes have almost identical properties. The *oxime* of pentane-3 : 4 : 5-triolal (metasaccharopentose) forms thin, prismatic crystals, less soluble than sodium chloride, m. p. 135—136°, $[\alpha]_D + 10·6°$; the *oxime* of pentane-1 : 4 : 5-triol-3-one (parasaccharopentose) has m. p. 136—137°, $[\alpha]_D + 11·8°$. The pentanetriolal is readily reduced to pentane-1 : 2 : 3 : 5-tetrol,

$$OH·CH_2·CH(OH)·CH(OH)·CH_2·CH_2·OH,$$

by means of sodium amalgam; the use of calcium (Neuberg and Marx, this vol., i, 387) for this purpose being unsuccessful. The tetrol is a syrup, but its *tetrabenzoate* forms glistening needles, m. p. 85—86°, which, like benzoyldextrose, is resistant towards acids or alkali hydroxides, but readily hydrolysed by sodium ethoxide. The tetrol so regenerated is a hygroscopic syrup; $[\alpha]_D + 29°$. E. F. A.

Combined Sulphurous Acids. III. Dextrose-sulphurous Acid. WILHELM KERP and EMIL BAUR (*Chem. Zentr.*, 1907, ii, 971; from *Arb. Kais. Ges.-A.*, 1907, 26, 269—296. Compare this vol., i, 1010).—Two optically active stereoisomeric compounds, which are not mirror images of one another, are obtained by the interaction of sodium hydrogen sulphite and dextrose. The compound investigated up to the present is the less soluble salt; it is lævorotatory, and gradually changes in solution into the other isomeride until equilibrium is established, the solution then being dextrorotatory. From electrical conductivity measurements, it follows that the free acid belongs to the strong acids. The dissociation of the complex anion is but slightly decreased by the addition of dextrose, whereas the effect produced by an increase in the number of hydrogen sulphite ions is normal. The degree of dissociation of the complex in an acid solution is not much greater than in a neutral solution, neither does it increase to any great extent with a rise of temperature. The diminution in the rate of dissociation of the complex produced by the addition of acids is very great. The addition of acetaldehyde to an aqueous solution of dextrose-sulphurous acid results in the formation of acetaldehyde-sulphurous acid and the liberation of dextrose. W. H. G.

The Hydrolysis of Sugars. ROBERT J. CALDWELL (*Brit. Assoc. Report*, 1906, 76, 267—292).—The report contains an historical section and summary of the different conditions under which sugar is hydrolysed. The various theories put forward to account for the inverting action of acids are discussed, and the facts in favour of the addition theory are set forth in some detail. The report also contains a complete bibliography, and the matter which is arranged in chronological sequence in each section is dated systematically throughout.

G. T. M.

Diastasic Liquefaction of Starch. AUGUSTE FERNBACH and JULES WOLFF (*Compt. rend.*, 1907, 145, 261—263).—The diastasic liquefaction of starch is subject to the same influences as liquefaction under pressure (Abstr., 1906, i, 803, 804). N. H. J. M.

The Present Position of the Chemistry of the Gums. HENRY H. ROBINSON (*Brit. Assoc. Report*, 1906, 76, 227—232).—A summary of the investigations made on the nature of different gums.

G. T. M.

Complex Metal Ammonias. IV. Tetraethylenediamine-diaquotetrolcobaltodicobaltic Salts. ALFRED WERNER [and, in part, GUSTAV JANTSCH] (*Ber.*, 1907, 40, 4426—4434. Compare this vol., i, 482).—The salts obtained by the atmospheric oxidation of aqueous solutions of cobaltous salts in the presence of ethylenediamine are found on investigation, excluding water and oxygen, to have the composition $[Co_3En_4]X_4$, where En = ethylenediamine and X a univalent acid radicle. When treated with cold hydrochloric acid, no halogen is evolved, but 1 mol. of the salt yields 1 mol. of a cobaltous salt and 2 mols. of a *cis*-diaquodiethylenediaminecobaltic salt, $[(H_2O)_2CoEn_2]X_3$. The H_2O mols. in the 2 mols. of the diaquo-salt are not present as such in the parent substance, since these compounds do not react like diaquo-salts; however, the complex of the parent compound contains 4 atoms of oxygen, which must be present in four OH groups; consequently two $[(OH)_2CoEn_2]X$ residues must be employed in the building up of the molecule. Since the molecule is decomposed by hydrochloric acid as stated above, it follows that these compounds are formed by the combination of 1 mol. of a cobaltous salt with 2 mols. of a dihydroxodiethylenediaminecobalt salt, $CoX_2 + 2[(HO)_2CoEn_2]X$. They, however, contain, in addition, 2 mols. of water retained by them in the dried state (the function of which is not yet known), and, as in solution the whole of the acid radicle is ionised, the following constitutional formula is assigned to these salts, which are consequently named *tetraethylenediaminediaquotetrolcobaltodicobaltic salts*, $\left\{Co''\begin{matrix}(H_2O)_2\\ [(HO)_2CoEn_2]_2\end{matrix}\right\}X_4$.

It is pointed out that cobaltous-cobaltic hydroxide, $Co_3(OH)_8$, probably has a similar constitution.

A solution of cobalt chloride containing ethylenediamine yields, on exposure to the air and subsequent treatment with common salt, a precipitate containing the *chloride* of the series and triethylenediaminecobalt chloride. The latter compound is removed by treating the precipitate with water, leaving the former as a bright red, slightly blue powder. This is converted by sodium sulphate into the *sulphate*, $\left\{Co\begin{matrix}(H_2O)_2\\ [(HO)_2CoEn_2]_2\end{matrix}\right\}(SO_4)_2{\cdot}5H_2O$, crystallising in bright red, microscopic needles. A solution of cobalt sulphate containing ethylenediamine deposits, on exposure to the air, the sulphate in the form of red needles. It cannot be recrystallised, being sparingly soluble in water, but, when treated with barium chloride and then with sodium sulphate, a *sulphate* similar to the above, but containing $7H_2O$, is obtained. The following salts are similarly obtained from the chloride by double decomposition: *dithionate*, $Co_3C_8H_{38}O_{18}N_8S_4,2H_2O$, a bluish-red powder; *platinichloride*, $Co_3C_8H_{38}O_6Cl_8Pt_2,3H_2O$, a light brownish-red, crystalline powder; *iodide*, $Co_3C_8H_{38}O_6N_8I_4,2H_2O$, a brownish-red, crystalline powder. W. H. G.

Action of Ammonia on the Oxides and Chlorohydrins of Hexylene and Tetramethylethylene [$\beta\gamma$-Dimethyl-Δ^{β}-butylene].

K. KRASSUSKY and L. DUDA (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1061—1076).—The tendency of α-olefine oxides to combine with ammonia does not depend so markedly on the structure of the oxide as is the case with its tendency to combine with water, and in so far as the former tendency does depend on the structure of the oxide it is the reverse of that of its combination with water. The first products obtained by the action of ammonia on the chlorohydrins of hexylene and $\beta\gamma$-dimethyl-Δ^{β}-butylene are the corresponding oxides, which are formed at quite low temperatures; consequently, in the formation of α-hydroxy-amines, the oxides are probably always intermediate products, and probably the whole of the α-hydroxy-amine formed from α-monochlorohydrin is identical with the amine obtained from the corresponding α-oxide.

α-Hexylene oxide is formed by heating hexylene with bleaching powder, and is best purified with 1% aqueous potassium permanganate. With aqueous ammonia in a sealed tube at 100°, the hexylene oxide yields: (1) a *secondary hydroxy-amine*, $(C_6H_{13}O)_2NH$; (2) *α-hydroxy-hexylamine*, $NH_2\cdot C_6H_{12}\cdot OH$, b. p. 189·5—190·5°/750 mm., D_0^0 0·9283, D_{20}^{20} 0·9141, which behaves as an alkali towards many reagents, and is also formed under similar conditions by hexylene chlorohydrin. The *platinichloride*, *hydrochloride*, and *carbonate* have been obtained in an impure form. With nitrous acid, the α-amine yields the same ketone as hexylene glycol.

βγ-Dimethyl-Δ^{β}-butylene oxide was obtained by distilling the corresponding chlorohydrin over potassium hydroxide. To form the α-amine, the oxide or chlorohydrin must be heated with a large excess of aqueous ammonia at 100°. The amine, $NH_2\cdot C_6H_{12}\cdot OH$, has b. p. 162—164°/756 mm., solidifies below 0°, and melts at 0—2° (Demjanoff: solid, 10°), readily absorbs carbon dioxide, forming a *carbonate*, and water, forming a crystalline *hydrate*, probably $NH_2\cdot C_6H_{12}\cdot OH,6H_2O$, m. p. 30—32°, which is also formed when the moist amine is distilled or mixed with water. On desiccation, the hydrate is transformed into the liquid amine. With the dry amine, nitrous acid produces pinacoline, but chiefly pinacone. Z. K.

Choline Cadmium Chloride. FRIEDRICH W. SCHMIDT (*Zeitsch. physiol. Chem.*, 1907, **53**, 428).—*Choline cadmium chloride*,

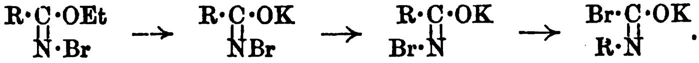
$$C_5H_{14}ONCl,CdCl_2,$$

is recommended as a substitute for the platinichloride in the preparation and purification of choline. It is thrown down as a crystalline precipitate on the addition of an alcoholic solution of cadmium chloride to an aqueous solution of choline chloride. J. J. S.

The Chemistry of Bile. II. Affinity Constant of Glycocholic Acid. SAMUEL BONDI (*Zeitsch. physiol. Chem.*, 1907, **53**, 8—13).—Pure glycocholic acid (Abstr., 1906, i, 633) is a comparatively strong acid. The dissociation constant, calculated from the results of electrical conductivity determinations with concentrations varying from 750—3000, is 0·0132. The value of μ_∞ calculated from the sodium salt is 363. The conclusion is drawn that in cholic acid the ·CH·OH group is not in the α-position with respect to the carboxyl group. J. J. S.

Formation of *iso*Serine from αβ-Dibromopropionic Acid. CARL NEUBERG and ERICH ASCHER (*Biochem. Zeitsch.*, 1907, **6**, 559—562).—In the preparation of αβ-diaminopropionic acid from αβ-dibromopropionic acid, a secondary reaction takes place, resulting in the formation of about 10% of *iso*serine, $NH_2\cdot CH_2\cdot CH(OH)\cdot CO_2H$. This reaction is analogous to the formation of methyl*iso*serine from αβ-dibromobutyric acid, described by Neuberg and Federer (Abstr., 1906, i, 805). G. B.

Formation of Amines from Halogen Imino-Ethers. MITSURU KUHARA and MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōto*, 1907, 1, 187—194. Compare Stieglitz, Abstr., 1903, i, 235; 1904, i, 39).—Stieglitz (*loc. cit.*) has shown that such compounds as chloro- and bromo-benzimino-ethyl ethers, $C_6H_5\cdot C(OEt)\!:\!NX$, do not undergo the Beckmann rearrangement, but yield with hydrochloric acid, ethyl benzoate and the corresponding halogen hypo-acid. The authors now find, however, that bromo- acetimino-, -propimino-, and benzimino-ethyl ethers on heating gently with potassium hydroxide and subsequently distilling, yield considerable amounts of the corresponding amines. As Stieglitz has shown that these esters probably have the *anti*-configuration, it is suggested that on saponification the potassium salts of the same form are obtained, which change to the more stable *syn*-form, undergo the Beckmann transformation, and then decompose under the influence of alkali, yielding amines as follows:



$$\begin{array}{c}R\cdot C\cdot OEt\\ \Vert\\ N\cdot Br\end{array} \longrightarrow \begin{array}{c}R\cdot C\cdot OK\\ \Vert\\ NBr\end{array} \longrightarrow \begin{array}{c}R\cdot C\cdot OK\\ \Vert\\ Br\cdot N\end{array} \longrightarrow \begin{array}{c}Br\cdot C\cdot OK\\ \Vert\\ R\cdot N\end{array}.$$

Aceto bromoimino-ethyl ether, $CH_3\cdot C(OEt)\!:\!NBr$, was obtained as an oily liquid by the action of potassium hypobromite on acetimino-ethyl ether. Besides the decomposition referred to above with concentrated alkali, it is split up on heating with water or hydrochloric acid, ethyl acetate and bromine distilling over. The corresponding *propionimino-ether* was obtained by an analogous method, and behaves like the acetate.

Benzobromoimino-ethyl ether, $C_6H_5\cdot C(OEt)\!:\!NBr$, already described by Stieglitz (*loc. cit.*), decomposes when in contact with water for some time, cyaphenine crystallising out, and bromine and ethyl benzoate being liberated. G. S.

Iminoacetic-α-propionic Acid. GEORGE STADNIKOFF (*Ber.*, 1907, 40, 4350—4353. Compare this vol., i, 393).—With the view of supporting the explanation previously given regarding the mode of formation of α-iminonitriles, the author has studied the synthesis of unsymmetrical imino-acids with the idea that these can be formed by the action of an oxynitrile on an aminonitrile or an ester of an amino-acid.

A concentrated aqueous solution of potassium cyanide was gradually added to a mixture of an aqueous solution of ethyl glycine hydrochloride and acetaldehyde. The mixture was subsequently saponified by hydrochloric acid, evaporated, and the salt of the imino-acid extracted with alcohol. After successive treatment with lead hydroxide and hydrogen sulphide, the aqueous solution of the imino-acid was concentrated. *Iminoacetic-α-propionic acid*,

$$CO_2H\cdot CHMe\cdot NH\cdot CH_2\cdot CO_2H,$$

separates from aqueous alcohol in large crystals, m. p. 222—223°. Its *copper* salt was prepared. Its *ethyl* ester is a colourless, viscid liquid, with b. p. 122·5°/12 mm., and D_4^{20} 1·0457; the ester forms a *nitroso*-derivative, $C_9H_{16}O_5N_2$, with b. p. 168—169°/13 mm., and D_4^{2} 1·1398. A. McK.

Imino-α-propionicbutyric Acid. GEORGE STADNIKOFF (*Ber.*, 1907, 40, 4353—4356. Compare preceding abstract).—Two optically inactive compounds of the formula $CO_2H\cdot CHMe\cdot NH\cdot CHEt\cdot CO_2H$ are theoretically possible. The author has prepared these two isomeric acids, one of which is formed in greater amount than the other; the acids can be separated by means of absolute alcohol.

By the interaction of acetaldehyde, potassium cyanide, and α-aminobutyronitrile hydrochloride (or ethyl α-aminobutyrate hydrochloride), the mixture of acids is obtained. The one, *imino-α-propionicbutyric acid*, which is the more sparingly soluble of the two in alcohol, crystallises in needles, m. p. 222—223° (decomp.); its *copper* salt was prepared. The *isomeric acid* could not be obtained crystalline, but was converted into its *copper* and *nickel* salts and its *ethyl* ester, $C_{11}H_{21}O_4N$, having b. p. 126°/16 mm., and D_4^{21} 1·0063. A. McK.

Aminocampholic Acids. HANS RUPE and J. SPLITTGERBER (*Ber.*, 1907, 40, 4311—4318).—The compound obtained by Oddo and Leonardi (Abstr., 1897, i, 86) by heating the hydrochloride of their so-called β-aminocampholic acid (which really belongs to the α-series) is identical with Tafel and Eckstein's α-camphidone (Abstr., 1902, i, 43). The authors find that the hydrochloride of α-aminocampholic acid has m. p. 247—248°, and is insoluble in light petroleum (Oddo and Leonardi, m. p. 268—270°, soluble in light petroleum); the *platinichloride*, $CO_2H\cdot C_8H_{14}\cdot CH_2\cdot NH_2,H_2PtCl_6$, separates from water in reddish-yellow leaflets.

β-Camphoramic acid, prepared from camphorimide and sodium hydroxide, contains the α-isomeride. A separation is readily effected by treating the alkaline solution of the sodium salts with hydrochloric acid; so long as the solution does not contain free mineral acid, β-camphoramic acid alone separates. By treatment with cold acetyl chloride, followed by the addition of the product to 12% ammonium hydroxide, it forms camphoro-β-mononitrile, which is reduced by sodium in dilute alcoholic solution to β-aminocampholic acid, of which the *hydrochloride* has m. p. 215—220° and yields β-camphidone above its m. p. or by treating its aqueous solution with solid sodium sulphite. The *carbamide*, $CO_2H\cdot C_8H_{14}\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, also yields β-camphidone above its m. p., 203—204°. By careful treatment with sodium nitrite in the cold, the hydrochloride of β-aminocampholic acid yields a yellow oil, which is converted by boiling barium hydroxide into the easily soluble *barium* salt, $(OH\cdot CH_2\cdot C_8H_{14}\cdot CO_2)_2Ba$, which on acidification yields a *lactone*, b. p. 121—122°/12 mm., which is probably β-campholide. C. S.

Preparation of Acetamide by the Action of Ammonium Hydroxide on Ethyl Acetate. ISAAC K. PHELPS and M. A. PHELPS (*Amer. J. Sci.*, 1907, [iv], 24, 429—432).—In a previous paper (Phelps and Deming, this vol., i, 832), it has been shown that, under certain conditions, a quantitative yield of formamide can be obtained from ethyl formate and ammonium hydroxide.

It is now shown that nearly theoretical quantities of acetamide can be obtained by leaving mixtures of ethyl acetate and strong solution of ammonia for about a fortnight. The reaction takes place more rapidly if a large excess of solution of ammonia is used, or if dry ammonia is passed into the mixture at −8° to −10° until it is saturated. E. G.

Preparation of α-Bromo*iso*valerylcarbamide. KNOLL & Co. (D.R.-P. 185962).—*α-Bromoisovalerylcarbamide*, leaflets, m. p. 149°, obtained by the action of α-bromo*iso*valeryl bromide or chloride on dry powdered carbamide at 70°, is a trustworthy hypnotic, which is quite free from the unpleasant secondary effects attending the therapeutic application of valeric and α-bromo*iso*valeric acids and their derivatives. G. T. M.

Preparation of Aliphatic Thiocyanates, Nitriles, and Nitro-compounds. PAUL WALDEN (*Ber.*, 1907, **40**, 4301. Compare this vol., i, 752).—A correction. The interaction of methyl sulphate with potassium cyanide, potassium nitrite, and potassium thiocyanate has already been studied by Kaufler and Pomeranz (Abstr., 1901, i, 634). E. F. A.

Dithiocyanatotetra-amminechromium Salts. PAUL PFEIFFER and M. TILGNER (*Zeitsch. anorg. Chem.*, 1907, **55**, 361—370. Compare this vol., ii, 694).—Complex salts of the type $[(SCN)_2Cr(NH_3)_4]X$, in which X represents Cl, Br, SCN, NO_3, $\frac{1}{2}SO_4$, have been prepared. The *thiocyanate* is obtained by warming an aqueous solution of chloro-aquotetra-amminechromium chloride, $[(OH_2)ClCr(NH_3)_4]Cl_2$, with excess of potassium thiocyanate; by the addition of hydrochloric or hydrobromic acid to the solution of this salt, the corresponding *chloride* and *bromide* are obtained. The *nitrate* is prepared from the chloride by precipitation with nitric acid, and the *sulphate* by rubbing the chloride with sulphuric acid.

The salts in question occur in small, brick-red to orange-red crystals, soluble in water with neutral reaction. The saturated solution of the chloride contains 2% of the salt.

On warming the chloride with ethylenediamine and then treating the resulting product in aqueous solution with potassium iodide, *triethylenediaminechromium iodide*, $\{Cr[C_2H_4(NH_2)_2]_3\}I_3,H_2O$, was obtained in yellow crystals.

Attempts to prepare compounds containing Cl_2 or Br_2 instead of $(SCN)_2$ in the nucleus have so far been unsuccessful. G. S.

Preparation of Dialkylbromoacetamides from Dialkylcyanoacetic Acids. PAUL HOERING (D.R.-P. 186739. Compare Abstr., 1905, i, 638).—The dialkylbromoacetamides, which are valuable hypnotics, are readily obtained from the dialkylcyanoacetic acids by successively converting these into dialkylacetonitriles, bromodialkylacetonitriles, and then by hydrolysis into the required amide. Diethylcyanoacetic acid when repeatedly distilled at 145—200°, or when heated under pressure, is converted into *diethylacetonitrile* [*pentane-γ-carboxylonitrile*], $CHEt_2\cdot CN$, b. p. 144°; *dipropylacetonitrile* [*heptane-δ-carboxylonitrile*], $CHPr^{\alpha}_2\cdot CN$, b. p. 183—184°, is a colourless liquid with an agreeable odour.

On bromination, the two preceding compounds yield respectively *bromodiethylacetonitrile*, colourless oil, b. p. 183—185°, and *bromodipropylacetonitrile*, b. p. 209—211°.

Bromodiethylacetamide, $CHEt_2\cdot CONH_2$, m. p. 64—65°, is prepared by hydrolysing the corresponding acetonitrile with concentrated sulphuric acid on the water-bath. G. T. M.

Action of Diazo-derivatives of Aliphatic Compounds on Cyanogen and its Derivatives. IV. and V. Hydrocyanic Acid. ALBERTO PERATONER and F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 432—441, 501—513. Compare this vol., i, 979).—According to von Pechmann (Abstr., 1895, i, 328, 493), the action of diazomethane on hydrocyanic acid yields acetonitrile. The authors, who have studied the interaction of these compounds in the gaseous state and in ethereal solution, and also the action of gaseous diazomethane on liquid hydrogen cyanide, find that acetonitrile is only a secondary product of the reaction, and is always accompanied by methylcarbylamine; no trace of a triazole derivative is obtained. The previous results indicate that, with a hydrogen cyanide of normal structure, the synthesis of osotriazole should take place with great readiness.

The literature dealing with the structure and tautomerism of hydrocyanic acid is discussed. T. H. P.

The Study of Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, jun., MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1906, 76, 257—267).—A résumé of recent work on hydroaromatic substances, containing also references to a comparative study of dihydrolaurolene, dihydro*iso*laurolene, and 1 : 1-dimethyl*cyclo*hexane, and to the action of phosphorus pentachloride on trimethyldihydroresorcin. G. T. M.

Reduction of Trimethylene [*cyclo*Propane]. RICHARD WILLSTÄTTER and JAMES BRUCE (*Ber.*, 1907, 40, 4456—4459).—Whilst ethylene is reduced by hydrogen and nickel at 30—45°, *cyclo*butane is reduced to butane only at 180° (following abstract). It is now found that *cyclo*propane, which in its constitution lies between ethylene and *cyclo*butane, is reduced to propane at an intermediate temperature, the reduction commencing at 80° and taking place rapidly at 120°. Contrary to Wolkoff and Menschutkin's statement (Abstr., 1899, i, 196, 321; 1900, i, 423), pure *cyclo*propane is readily obtained by the action of zinc dust on trimethylene dibromide (Gustavson, Abstr., 1899, i, 421). G. Y.

Derivatives of *cyclo*Butane. II. RICHARD WILLSTÄTTER and JAMES BRUCE (*Ber.*, 1907, 40, 3979—3999).—*cyclo*Butene, prepared by distillation of trimethyl*cyclo*butylammonium hydroxide, contains up to 10% of $\Delta^{\alpha\gamma}$-butadiene. As was shown previously (Willstätter and Schmaedel, Abstr., 1905, i, 514), these hydrocarbons yield dibromides which can be separated by treatment with dimethylamine when $\alpha\delta$-butadiene dibromide is converted into $\alpha\delta$-tetramethyldiamino-

Δ$^{\beta}$-butylene, *cyclo*butene dibromide remaining unchanged. Pure *cyclo*butene is now obtained by reduction of its dibromide with zinc dust and alcohol; on reduction by means of finely-divided nickel and hydrogen (Sabatier and Senderens, Abstr., 1905, i, 333, 401) at 100°, it yields *cyclo*butane, whilst, when reduced at 180—200°, it forms butane. Attempts to prepare *cyclo*butene by distillation of amino-*cyclo*butane phosphate (Harries, Abstr., 1901, i, 194) led to the formation of butadiene. The preparation of *cyclo*butane completes the series *cyclo*propane–*cyclo*nonane; a table is given showing the rise of the b. p., m. p., D^0_4, and mol. vol. at 0° throughout the series. The mol. vols. of two neighbouring members of the series differ on the average by 13, except in the case of the last pair, the mol. vol. of *cyclo*nonane exceeding that of *cyclo*octane by 28·54. The molecular refractions of all members of the series to *cyclo*octane, so far as observed, agree with those calculated, whereas that observed for *cyclo*nonane (Zelinsky, this vol., i, 780) exceeds the calculated by 0·75.

*cyclo*Butene, b. p. 1·5—2°/729 mm., D^0_4 0·733, has a slight odour, dissolves readily in acetone, is absorbed by caoutchouc, reduces potassium permanganate instantaneously, and forms additive compounds rapidly with chlorine and bromine, but slowly with iodine.

cyclo*Butylamine phosphate*, $C_4H_7\cdot NH_2,H_3PO_4$, crystallises in prisms, m. p. 177—179°. The action of bromine on the product obtained on distilling the phosphate leads to the formation of the two stereoisomeric butadiene tetrabromides, m. p. 118° and 40—41° (Ciamician and Magnaghi, Abstr., 1886, 521), or of butadiene dibromide.

cyclo*Butane*, C_4H_8, b. p. 11—12°/760 mm. (corr.), remains liquid at −80°, D^0_4 0·703, D^{-5}_4 0·718, n^0_D 1·37520, has a slight odour, burns with a luminous flame, and is stable towards concentrated hydriodic acid or bromine in chloroform solution at the ordinary temperature. Butane, formed by reduction of *cyclo*butene, *cyclo*butane, or ψ-butylene by means of hydrogen and nickel at 180—200°, has b. p. −4° to −1·5°/722 mm.

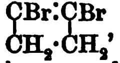
cyclo*Butene dichloride*, $C_4H_6Cl_2$, is a colourless liquid, b. p. 133·5—134·5°/760 mm. (corr.), D^0_4 1·235, D^{20}_4 1·213, and is not inflammable, but imparts a green colour to a bunsen flame. cyclo*Butene di-iodide* crystallises in plates, m. p. 48°, D^{20}_4 2·659, has an odour of camphor, and commences to dissociate at 140°.

The tendency of the *cyclo*butane derivatives to yield acyclic compounds, especially in reactions at high temperatures, is well known. It is now shown that *cyclo*butene dibromide and dichloride do not react with bromine alone even when heated, but, with bromine in presence of iron, *cyclo*butene dibromide yields *ααδδ-(or ααβδ-)tetrabromobutane*, which is obtained as a colourless oil, b. p. 138—145°/10 mm., D^0_4 2·562, D^{20}_4 2·529, n^{20}_D 1·60771, and on further bromination in presence of iron loses hydrogen bromide, forming an oily product containing small amounts of hexabromo*cyclo*butane, and when heated with alcoholic potassium hydroxide yields a *product*, $C_4H_4Br_2$, b. p. 47—48°/14 mm., D^0_4 1·99. This is readily oxidised by potassium permanganate, forms an *additive* compound with 1 mol. of bromine, and is probably a *cyclo*propane derivative.

The action of bromine on *cyclo*butene dichloride in presence of iron leads to the formation of *dichlorodibromobutane*, b. p. 120—125°/13 mm., D^{20}_{4} 2·1, *dichlorotribromobutane*, b. p 155—157°/18 mm., D^{0}_{4} 2·47, which is the chief product, and *dichlorotetrabromobutane*, b. p. 176—185°/21 mm., D^{0}_{4} 2·69.

Whilst *cyclo*butene dibromide does not react with bromine in presence of iodine, *cyclo*butene di-iodide reacts with bromine alone, yielding tetrabromobutane.

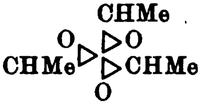
a-Bromobutadiene, $CHBr{:}CH{\cdot}CH{:}CH_2$, formed together with a small amount of *hydrocarbon*, which gives a white precipitate with silver nitrate by the action of potassium hydroxide on *aδ*-butadiene dibromide, is obtained as a mobile liquid, b. p. 92—94°/760 mm. (corr.), D^{0}_{4} 1·416, has an odour of vinyl bromide, and gradually changes into a sparingly soluble, dark brown mass, probably a polymerisation product. *a*-Bromobutadiene combines slowly with 2 mols. of bromine, forming *aaβγδ-pentabromobutane*, $C_4H_5Br_5$, which is a colourless oil, b. p. 165—170°/10 mm. D^{0}_{4} 2·78, and consists of a mixture of two crystalline *isomerides*, which form prisms, m. p. 108°, and plates, m. p. 57—58°, respectively.

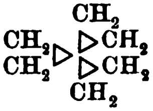
1 : 1-Dibromo*cyclo*butane, $C_4H_6Br_2$, b. p. 157—158·5°/760 mm. (corr.), D^{0}_{4} 1·960, D^{20}_{20} 1·933, n^{20}_{D} 1·53618 (Kijner, Abstr., 1905, i, 355), is prepared by the action of hydrogen bromide on bromo-Δ¹-*cyclo*butene in glacial acetic acid solution. 1 : 1 : 2-*Tribromo*cyclo*butane*, $C_4H_5Br_3$, formed by the action of bromine on bromo-Δ′-*cyclo*butene in chloroform solution, is a colourless oil, b. p. 109—110°/19—20 mm., D^{0}_{4} 2·374, has an odour of camphor, is volatile in a current of steam, and when treated with methyl-alcoholic potassium hydroxide yields 1 : 2-*dibromo*- Δ¹-cyclo*butene*,  $\begin{array}{l}CBr{:}CBr\\ |\qquad\quad |\\ CH_2{\cdot}CH_2\end{array}$, which is obtained as an oil, b. p. 155—156°, D^{0}_{4} 2·036, has an odour of vinyl bromide, gradually polymerises, and on oxidation with permanganate in neutral solution yields succinic acid.

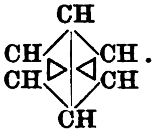
1 : 1 : 2 : 2-*Tetrabromo*cyclo*butane*, $C_4H_4Br_4$, formed by the action of bromine on 1 : 2-dibromo-Δ¹-*cyclo*butene in chloroform solution, crystallises in hexagonal plates, m. p. 126°, distils unchanged in a vacuum, and yields 1 : 2-dibromo-Δ¹-*cyclo*butene when heated with methyl-alcoholic potassium hydroxide. A mixture of this tetrabromo*cyclo*butane with the somewhat similar *a*-butadiene tetrabromide has m. p. about 50°.

1 : 1 : 2 : 2 : 3-*Pentabromo*cyclo*butane*, $C_4H_3Br_5$, formed by the action of bromine and iron powder on tetrabromo*cyclo*butane, is a colourless oil, b. p. 175—185°/19 mm., D^{20}_{4} 2·88, has a terpene odour, and on treatment with bromine and iron powder at 50—80° yields 1 : 1 : 2 : 2 : 3 : 4-*hexabromo*cyclo*butane*, $C_4H_2Br_6$, which crystallises from benzene in plates, m. p. 186·5° (corr.), and decomposes, evolving bromine, when heated in a tube. This hexabromo-compound closely resembles Sabanéeff's hexabromotetramethylene, m. p. 183·3° (corr.) (Noyes and Tucker, Abstr., 1897, i, 261). G. Y.

Improbability of Kekulé's Hypothesis. Raymond Vidal (*Chem. Zentr.*, 1907, i, 1787; from *Mon. sci.*, 1907, [iv], 21, i, 244—249).—The author discusses the known objections to Kekulé's benzene formula, and maintains that the formation of aromatic from aliphatic compounds, for example, paraldehyde from acetaldehyde and hexahydrobenzene and benzene from ethylene, is better understood by the use of such formulæ as the following:







W. H. G.

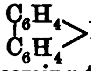
Cerium Salts of Certain Organic Acids. GILBERT T. MORGAN and EDWARD CAHEN (*Pharm. J.*, 1907, 78, 428—430. Compare Trans., 1907, 91, 475).—*Cerous naphthalene*-2 : 7-*disulphonate*, $Ce[C_{10}H_6(SO_3)_2]_3,25H_2O$, crystallises in small, nacreous leaflets having a pink colour; the water of crystallisation is only removed completely at 160°. *Cerous* 4-*nitrotoluene*-2-*sulphonate*, $Ce[C_6H_3Me(NO_2)SO_3]_6,10H_2O$, crystallises in yellow plates and intumesces on heating, leaving a bulky residue of ceric oxide. *Cerous* iso*valerate*, $Ce_2(C_5H_9O_2)_6,5H_2O$; *benzoate*, $Ce_2(C_7H_5O_2)_6$; *cinnamate*; o-*coumarate*; *succinate*, $Ce_2(C_4H_4O_4)_3,5H_2O$, and *camphorate*, $Ce_2(C_{10}H_{14}O_4)_3,9H_2O$, are white, amorphous or microcrystalline powders, very sparingly soluble in water. *Cerous salicylate*, $Ce_2(C_7H_5O_3)_6,3H_2O$, is soluble in water, and crystallises from a hot solution in stellate groups of small, light needles having a pale mauve tinge. *Cerous lactate* is very soluble; when its aqueous solution is dehydrated over sulphuric acid, it solidifies to a crystalline mass, the composition of which corresponds with a salt containing $7H_2O$. *Cerous oleate*, prepared by stirring precipitated cerous hydroxide and oleic acid together, is a buff-coloured substance having the consistence of lard.

H. M. D.

Preparation of Aromatic Fluoro-compounds by Decomposing Diazo- and Bisdiazo-compounds with Concentrated Hydrofluoric Acid. VALENTINER and SCHWARZ (D.R.-P. 186005).—The methods for obtaining fluoro-derivatives of the aromatic hydrocarbons have hitherto only furnished small yields of the products. It is now found that the diazo-fluoride produced by adding hydrofluoric acid to a solution of the diazo- or bisdiazo-chloride is readily decomposed catalytically by ferric chloride, yielding the aromatic fluoro-derivative. 4 : 4′-Difluorodiphenyl is produced on adding successively concentrated hydrofluoric acid and 10% ferric chloride solution to a solution of bisdiazodiphenyl chloride. The fluoro-derivatives of benzene, cumene, and naphthalene may be obtained similarly.

G. T. M.

Derivatives of Diphenyleneiodonium Hydroxide: New Class of Heterocyclic Compounds containing Iodine in the Closed-Chain. LUIGI MASCARELLI (*Atti R. Accad. Lincei.*, 1907, [v], 16, ii, 562—567).—By treating di-iodoxydiphenyl or di-iodosodiphenyl with moist silver oxide (compare Hartmann and Meyer, Abstr., 1894, i, 242), the author has obtained diphenylene-



iodonium hydroxide, $\left.\begin{array}{l}C_6H_4\\ C_6H_4\end{array}\right>I\cdot OH$, closure of the ring being effected by the iodine atom becoming tervalent.

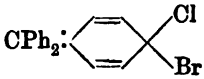
o-*Di-iododiphenyl*, $C_6H_4I\cdot C_6H_4I$, prepared by diazotising-*o*-diaminodiphenyl and decomposing the diazo-compound with potassium iodide, separates from water as a pale yellow, microcrystalline powder, m. p. 210—211°. Its *tetrachloride*, $C_6H_4Cl_2I\cdot C_6H_4Cl_2I$, separates from chloroform in yellow, acicular crystals, m. p. 130—135° (decomp.).

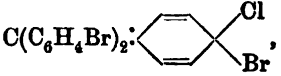
o-*Di-iodosodiphenyl*, $OI\cdot C_6H_4\cdot C_6H_4\cdot OI$, obtained by the action of dilute potassium hydroxide solution on *o*-di-iododiphenyl tetrachloride, is a yellow, amorphous powder, m. p. 109—110°.

o-*Di-iodoxydiphenyl*, $IO_2\cdot C_6H_4\cdot C_6H_4\cdot IO_2$, obtained on boiling *o*-di-iodosodiphenyl with water, forms slender, white crystals, m. p. 280°.

Diphenyleneiodonium hydroxide, crystallising in slender, white filaments, m. p. 145—148° (decomp.), was not analysed. The *acetyl* derivative, $I(C_6H_4)_2Ac$, crystallises in hard, white prisms, m. p. 195·5° (decomp.), and has the normal molecular weight in freezing ethylurethane. The *oxalate*, $C_2O_4[I(C_6H_4)_2]_2$, crystallises from water in colourless prisms, m. p. 191—192°. T. H. P.

Problem of the Structural Formula of "Triphenylmethyl." ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1907, 40, 3965—3970).—The author criticises Gomberg's quinonoid theory of the coloured salts derived from triphenylcarbinol (this vol., i, 504) from the same point of view as does Baeyer (this vol., i, 691). When treated with water, the strongly coloured double salts of stannic chloride and *p*-bromo- and tri-*p*-bromo-triphenylmethyl chlorides yield hydrogen chloride, but not even traces of hydrogen bromide. In the same manner, no trace of alkali bromide is obtained together with the alkali chloride when *p*-bromo- and tri-*p*-bromo-triphenylmethyl chlorides are heated with sulphur dioxide at 50° and subsequently with an aqueous alkali, whereas if the coloured salts had the quinonoid structures annexed:





the isomerisation would lead to the formation of mixtures of carbinyl chlorides and bromides and hence of alkali chlorides and bromides.

Schmidlin's supposed isomeric magnesium triphenylmethyl chlorides (this vol., i, 26) are criticised. Both the α- and β-modifications react with benzoyl chloride and ethyl benzoate, forming benzopinacolin in an 80% yield. Contrary to Schmidlin's statement, the α-modification on treatment with carbon dioxide in ethereal solution yields triphenylacetic acid in a 90% yield; the action of water on the reaction product leads to the formation of triphenylmethane in good yields. The *p*-benzoyltriphenylmethane obtained by Schmidlin is formed most probably by condensation of triphenylmethane with benzaldehyde.

G. Y.

Phenanthrene Series. XXI. Hydrophenanthrenes. JULIUS SCHMIDT and ROBERT MEZGER (*Ber.*, 1907, 40, 4240—4257).—Only two hydrophenanthrenes have been referred to previously, namely, α-tetrahydrophenanthrene (Bamberger and Lodter, Abstr., 1888, 292) and octohydrophenanthrene (Graebe, Abstr., 1873, 894). By using different methods and conditions of reduction, the authors have succeeded in preparing a number of hydrogenated derivatives comprised between the limiting di- and dodeca-hydrophenanthrenes. The lower members of this series are obtained by means of sodium and amyl alcohol, and the higher ones by means of phosphorus and hydriodic acid. In order to obtain pure products and not mixtures of various hydro-derivatives difficult to resolve into their constituents, it is necessary to adhere closely to the conditions laid down by the authors. The experiments of Liebermann and Spiegel (Abstr., 1889, 719) have been repeated, the results indicating that the perhydrophenanthrene described by these authors does not exist.

9 : 10-*Dihydrophenanthrene*, $C_{14}H_{12}$, prepared either by the action of sodium and amyl alcohol on phenanthrene or by passing a mixture of hydrogen and phenanthrene vapour over reduced nickel at 200°, crystallises from alcohol in shining, snow-white leaflets, m. p. 94—95°, b. p. 312—314°/739 mm., and closely resembles phenanthrene in its solubility and other properties. It is not acted on by bromine, but yields a *picrate*, $C_{14}H_{12},C_6H_3O_7N_3$, forming brick-red needles, m. p. 135—137°. On oxidation, it yields phenanthraquinone in almost theoretical proportion.

α-Tetrahydrophenanthrene [2 : 7 : 9 : 10- or 4 : 5 : 9 : 10-tetrahydrophenanthrene], $C_{14}H_{14}$ (compare Graebe, *loc. cit.* and Bamberger, *loc. cit.*), is a colourless oil, b. p. 307°/317 mm., m. p. $-4°$ to $-5°$, D^{20}_{4} 1·080, n^{20}_{D} 1·5820. It gives a *picrate*, $C_{14}H_{14},C_6H_3O_7N_3$, forming orange-red needles, m. p. 105—106°.

β-Tetrahydrophenanthrene [2 : 7 : 9 : 10- or 4 : 5 : 9 : 10-tetrahydrophenanthrene], $C_{14}H_{14}$, is a yellow oil, b. p. 302—303°/737 mm., m. p. $-3°$ to $-4°$, D^{20}_{4} 1·085, n^{20}_{D} 1·5820, more stable to the action of air and light than the α-derivative, and yields no picrate.

Hexahydrophenanthrene, $C_{14}H_{16}$, is a colourless oil, b. p. 289—290°/737 mm., m. p. $-7°$ to $-8°$, D^{20}_{4} 1·045, n^{20}_{D} 1·5704, and yields no picrate.

Octohydrophenanthrene (compare Graebe, *loc. cit.*), $C_{14}H_{18}$, is a colourless oil, b. p. 282°/737 mm., m. p. $-11°$ to $-12°$, D^{20}_{4} 1·012, n^{20}_{D} 1·5599 ; it does not form a picrate.

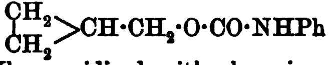
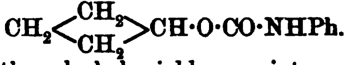
Decahydrophenanthrene, $C_{14}H_{20}$, is a colourless oil, b. p. 274—275°/737 mm., m. p. $-18°$ to $-20°$, D^{20}_{4} 0·993, n^{20}_{D} 1·5335 ; it does not yield a picrate.

Dodecahydrophenanthrene, $C_{14}H_{22}$, is obtained as a colourless oil, b. p. 268—269°/737 mm., D^{20}_{4} 0·964, n^{20}_{D} 1·5119, remaining liquid at $-20°$; it gives no picrate.

No more highly hydrogenated derivative than the dodecahydrocompound could be prepared. T. H. P.

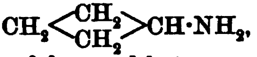
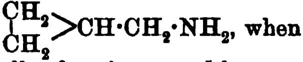
Isomerisation of Cyclic Amines containing the Side-chain $CH_2\cdot NH_2$. The Nature of the Alcohol obtained from the Amine: $\left.\begin{array}{l}CH_2\\ CH_2\end{array}\right>CH\cdot CH_2\cdot NH_2$.

Nicolaus J. Demjanoff (*Ber.*, 1907, **40**, 4393—4397; *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1077—1085).—The amine and its corresponding alcohol were prepared as described previously (*ibid.*, 1905, **37**, 622), some modifications being introduced in the formation of the nitrile, $\genfrac{}{}{0pt}{}{CH_2}{CH_2}\!>CH\cdot CN$. The phenylurethane, prepared from the alcohol, is a mixture of the two compounds:


$\genfrac{}{}{0pt}{}{CH_2}{CH_2}\!>CH\cdot CH_2\cdot O\cdot CO\cdot NHPh$ and

$CH_2\!<\!\genfrac{}{}{0pt}{}{CH_2}{CH_2}\!>CH\cdot O\cdot CO\cdot NHPh$.

When oxidised with chromic acid, the alcohol yields a mixture of aldehydes, which form two semicarbazones, one of which,

$C_4H_6{:}N\cdot NH\cdot CO\cdot NH_2$,

m. p. 125—126°, is soluble in ether, the other has m. p. 202·5—203°, is insoluble in ether, and is identical with the one obtained from the alcohol prepared from amino*cyclo*butane,  $CH_2\!<\!\genfrac{}{}{0pt}{}{CH_2}{CH_2}\!>CH\cdot NH_2$, and probably also with Kijner's semicarbazone of keto*cyclo*butane. The alcohol is also oxidised readily with nitric acid, forming much succinic acid, whilst the pure *cyclo*propyl carbinol yields only traces of succinic acid. It is thus evident that, contrary to Dalle's statement (Abstr., 1902, i, 525), the amine,  $\genfrac{}{}{0pt}{}{CH_2}{CH_2}\!>CH\cdot CH_2\cdot NH_2$, when converted into an alcohol, isomerises partially, forming a *cyclo*butane derivative.

Z. K.

Preparation of Derivatives of Formaldehydesulphoxylic Acid containing Nitrogen. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 185689. Compare Abstr., 1906, i, 480).—A mixture of aniline, sodium formaldehydesulphoxylate, and water is heated at 70—80° until the base has dissolved. The solution when concentrated under diminished pressure yields a deposit of acicular crystals of a new compound of aniline and the sulphoxylate. This substance decomposes in the dry state, but is stable in the form of a paste. The homologues of aniline yield similar products, and a corresponding compound of ammonia may be obtained as a white, porcelain-like mass, which differs from the original formaldehydesulphoxylate in being insoluble in methyl alcohol. The aliphatic amines give rise to similar compounds. These formaldehydesulphoxylate derivatives are powerful reducing agents, and may be employed in the printing of textile fabrics. They reduce indigo-carmin on warming, or even in the cold in the presence of mineral acids. When warmed with aqueous sodium hydroxide, these new compounds are reconverted into their generators.

G. T. M.

Derivatives of *m*-Iodonitrobenzene, *m*-Iodoaniline, and *m*-Iodoacetanilide containing Multivalent Iodine. CONRAD WILLGERODT and E. HJALMAR WIKANDER (*Ber.*, 1907, **40**, 4066—4069).—The following salts of di-*m*-nitrophenyliodinium hydroxide are described. The *chloride*, m. p. 214°, white needles; *bromide*, white powder, decomposing at 183—184°; *iodide*, m. p. 130·5° (decomp.), yellowish-white powder; *periodide*, $(C_6H_4\cdot NO_2)_2I,I_3$, m. p. 127° (decomp.), dark brown needles, obtained from the preceding salt and alcoholic iodine; *platinichloride*, $2(C_6H_4{\cdot}NO_2)_2I,PtCl_6$, m. p. 196—197° (decomp.), dark brown needles; *nitrate*, m. p. 194°, white needles; *hydrogen sulphate*, m. p. 168·5°; *dichromate*, yellow powder, exploding at 163°.

m-*Nitrodiphenyliodinium chloride*, $NO_2{\cdot}C_6H_4{\cdot}IPhCl$, m.p. 170—172°, is obtained by triturating *m*-nitrophenyl iododichloride and mercury diphenyl under water; the *mercurichloride* has m. p. 152°; the *platinichloride* decomposes at 177°; the *iodide* at 153°, and the *periodide*, $NO_2{\cdot}C_6H_4{\cdot}IPh,I_3$, has m. p. 118° (decomp.).

Iodoso-, iodoxy-, and iodinium compounds have not yet been isolated from iodoanilines.

m-*Acetylaminophenyl iododichloride*, $NHAc{\cdot}C_6H_4{\cdot}ICl_2$, is obtained in yellow crystals by passing chlorine into a solution of *m*-iodoacetanilide in glacial acetic acid at 0°, but not in chloroform; it decomposes at 66°, and by treatment with a solution of sodium carbonate is converted into m-*iodosoacetanilide*, which decomposes at 72°. C. S.

Derivatives of *p*-Iodoacetanilide containing Multivalent Iodine, and *p*-Aminodiphenyliodinium Compounds. CONRAD WILLGERODT and WALTER NÄGELI (*Ber.*, 1907, 40, 4070—4077. Compare preceding abstract).—p-*Acetylaminophenyl iododichloride*, $NHAc{\cdot}C_6H_4{\cdot}ICl_2$, m. p. 110° (decomp.), prepared in the usual manner, forms very stable yellow needles. Cold sodium carbonate solution converts it into p-*iodosoacetanilide*, which decomposes at 114°, and forms with potassium dichromate a yellow basic *chromate*,

$$(OH{\cdot}I{\cdot}C_6H_4{\cdot}NHAc)_2CrO_4,$$

which decomposes at 85—90°. p-*Iodoxyacetanilide*, $NHAc{\cdot}C_6H_4{\cdot}IO_2$, prepared from the iodoso-compound and a small excess of sodium hypochlorite solution, the reaction being accelerated by the addition of a few drops of glacial acetic acid, explodes at 163°.

p-*Acetylaminodiphenyliodinium hydroxide*, $NHAc{\cdot}C_6H_4{\cdot}IPh{\cdot}OH$, is obtained in aqueous solution from iodoxybenzene and *p*-iodosoacetanilide in the usual manner, or by decomposing the iodinium chloride with moist silver oxide. The *chloride*, m. p. 190°, is prepared from the hydroxide, or from mercury diphenyl and *p*-acetylaminophenyl iododichloride. The *bromide* has m. p. 183°; the *iodide*, m. p. 174°; the *periodide*, m. p. 145° (decomp.); *nitrate*, m. p. 180·5°; *dichromate*, decomp. 60°; *platinichloride*, m. p. 166°; *mercurichloride*, decomp. 109°.

Di-p-*acetylaminophenyliodinium hydroxide*, $(NHAc{\cdot}C_6H_4)_2I{\cdot}OH$, forms the following salts. The *chloride* is too soluble to be isolated in the crystalline state. The *bromide*, m. p. 165°; the *iodide*, m. p. 176·5°; *dichromate*, m. p. 176° (decomp.); *platinichloride*, m. p. 162° (decomp.); *mercurichloride*, m. p. 162°. p-*Acetylaminophenyl*-p-*tolyliodinium hydroxide* forms the salts: *chloride*, m. p. 204·5°; *bromide*, m. p. 185°; *iodide*, m. p. 157°; *dichromate*, m. p. 140° (decomp.); *platinichloride* begins to decompose at 159°, and then has m. p. 178°; *mercurichloride*, m. p. 145°.

Hydrolysis of *p*-acetylaminodiphenyliodinium chloride takes place when the substance is heated with 10% alcoholic hydrogen chloride for one hour on the water-bath, the products being ethyl acetate and the *hydrochloride* of p-*aminodiphenyliodinium chloride*,

$$NH_2\cdot C_6H_4\cdot IPhCl,HCl.$$

The corresponding *platinichloride*, $NH_2\cdot C_6H_4\cdot IPh\cdot HPtCl_6$, prepared from a strongly acidified solution of the iodinium chloride and excess of platinic chloride, crystallises in small needles, m. p. 194° (decomp.).

The *platinichloride*, $2NH_2\cdot C_6H_4\cdot IPh,PtCl_6$, is a yellow, crystalline precipitate obtained by adding platinic chloride to an aqueous solution of the iodinium chloride, and decomposes above 240°. The *bromide* has m. p. 182·5°; the *iodide*, m. p. 164°; the *dichromate* blackens at 130°, and has m. p. 143° (decomp.).

Azo-compounds are obtained in an impure state from a diazotised solution of *p*-aminodiphenyliodinium bromide and *β*-naphthol or *R*-salt. C. S.

Derivatives of *p*-Iododiphenyliodinium Chloride and of Iodoaceto-*o*-toluidide containing Multivalent Iodine. Preparation of Chloroacylamines containing Iodine.

CONRAD WILLGERODT and KARL HEUSNER (*Ber.*, 1907, 40, 4077—4085).—Meyer and Hartmann's *p*-iododiphenyliodinium iodide can be prepared by treating the diazotised solution of the hydrochloride of *p*-aminodiphenyliodinium chloride (preceding abstract) with a solution of potassium iodide (2 mols.); it has m. p. 145°; the *bromide* has m. p. 166°.

*Iodoaceto-*o*-toluidide*, $NHAc\cdot C_7H_6I$, m. p. 169·5°, is obtained from aceto-*o*-toluidide and iodine monochloride in glacial acetic acid. The position of the halogen is not yet determined, but it is probably para to the acetylamino-group. The following compounds are prepared by the usual methods: o-*acetylaminotolyl iododichloride*,

$$NHAc\cdot C_7H_6\cdot ICl_2,$$

forms stable yellow crystals and decomposes at 109°; the *iodoso*-compound is very unstable, and the iodoxy-compound has not been isolated. *Phenyl-*o*-acetylaminotolyliodinium hydroxide* forms a *chloride*, m. p. 179°; *bromide*, m. p. 173·5°; *iodide*, m. p. 152°; *dichromate*, decomposing at 65°; *platinichloride*, beginning to decompose at 100°, and m. p. 135° (decomp.).

The *hydrochloride* of *phenyl-*o*-aminotolyl iodinium chloride*,

$$NH_2\cdot C_7H_6\cdot IPhCl,HCl,$$

is obtained by hydrolysing the preceding iodinium chloride by 10% alcoholic hydrogen chloride; it begins to decompose at 150°, and has m. p. 255° (decomp.). The *bromide*, $NH_2\cdot C_7H_6\cdot IPhBr$, has m. p. 175°; the *iodide*, m. p. 169°; *dichromate*, decomp. 155°; *platinichloride*, m. p. 157° (decomp., beginning at 120°).

*Iodoxy-*o*-acetylchloroaminotoluene*, $NClAc\cdot C_6H_3Me\cdot IO_2$, is obtained from *o*-acetylaminotolyliododichloride and sodium hypochlorite in acetic acid solution; the composition is controlled by an estimation of the halogens and of the iodine liberated from potassium iodide. *Acetylchloroamino-*p*-iodoxybenzene*, $NClAc\cdot C_6H_4\cdot IO_2$, prepared in a similar manner, explodes at 158°. *Iodo-*o*-acetylchloroaminotoluene*,

$$NClAc\cdot C_6H_3Me\cdot I,$$

m. p. 92° (decomp., beginning at 85°), is obtained by adding slowly a solution of sodium hypochlorite to a not too concentrated solution of iodoaceto-*o*-toluidide in glacial acetic acid. *Acetylchloroamino*-p-*iodobenzene*, $NClAc\cdot C_6H_4\cdot I$, prepared in a similar manner, has m. p. 127° (decomp., beginning at 115°). C. S.

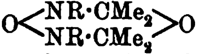
The Transformation of Aromatic Nitroamines and Allied Substances and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Ass. Report*, 1906, 76, 159—161).—A summary of the reactions of *s*-tribromonitroaminobenzene and of changes which lead to the displacement of halogen by hydroxyl in halogenated benzene diazo-compounds. G. T. M.

Preparation of *p*-Nitrodiphenylamine and its Derivatives. IRMA GOLDBERG (D.R.-P. 185663).—Although *p*-chloronitrobenzene and aniline do not interact alone, a mixture of the two compounds may be caused to condense by heating with potassium carbonate in the presence of a small proportion of cuprous iodide. Nitrobenzene may be employed as a diluent, and the aniline may be replaced by other aromatic amines. 4-*Nitrophenyl*-p-*tolylamine*, green crystals, m. p. 138°, was thus obtained from *p*-toluidine; 4 : 4′-dinitrodiphenylamine was produced from *p*-nitroaniline, *p*-chloronitrobenzene, potassium carbonate, and cuprous iodide when the mixture was heated for eighteen hours in boiling nitrobenzene. When the *p*-nitroaniline is replaced by anthranilic acid, 4-nitrophenylanthranilic acid, m. p. 211°, was obtained. G. T. M.

Beckmann's Rearrangement. MITSURU KUHARA and TADAKA KAINOSHÔ (*Mem. Coll. Sci. Eng. Kyôto*, 1907, 1, 254—264. Compare Beckmann, Abstr., 1894, i, 240).—Varying quantities of diphenylketoxime, dissolved in chloroform, were heated with a constant quantity of acetyl chloride for some hours at 100—110°, and it was found that the amount of benzanilide formed by the Beckmann rearrangement was proportional to the oxime concentration only; it is therefore suggested that the action of the acetyl chloride in the reaction is catalytic. Further, when a fixed amount of acetyldiphenylketoxime is heated for some time with varying proportions of hydrochloric acid in chloroform solution, the amount of benzanilide formed is approximately proportional to the concentration of acid. Chlorobenzylideneaniline, $NPh\colon CPhCl$, which may be an intermediate product in the Beckmann rearrangement, reacts immediately with a mixture of acetic anhydride and glacial acetic acid with formation of benzanilide and acetyl chloride.

On the basis of these results and of those of previous observers, it is suggested that the Beckmann rearrangement in the presence of acetyl chloride depends on the formation of an intermediate compound of acetyl chloride and the oxime, which undergoes rearrangement under the catalytic influence of the hydrochloric acid produced, the latter also taking a direct part in the final stage of the reaction, in which the substituted amide is produced and acetyl chloride regenerated.

G. S.

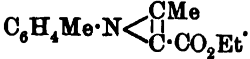
N-Alkylketoximes. JOHANNES SCHEIBER and HUBERT WOLF (*Annalen*, 1907, **357**, 25—48. Compare Beckmann and Scheiber, this vol., i, 829).—Aldehydes react with β-substituted hydroxylamines forming additive compounds which undergo intramolecular condensation to N-alkylaldoximes. It was to be expected that the products obtained from the action of β-substituted hydroxylamines on acetone and ethyl acetoacetate are formed in the same manner. A comparison of these substances with the N-alkylaldoximes leads to the conclusion that the first stage of the reaction is the formation of an additive compound; the further action, however, varies with the ketone and the β-substituted hydroxylamine. The condensation products of acetone and β-substituted hydroxylamines differ from the N-alkylaldoximes in that they decompose on fusion, are unstable in solution, have mol. weights double those corresponding with the formula $\mathrm{CRR''}<\begin{matrix}\mathrm{NR'}\\ |\\ \mathrm{O}\end{matrix}$, and are decomposed by phenylcarbimide and acid chlorides or anhydrides. The action of hydrogen chloride on N-alkylacetoximes in ethereal solution leads to the formation of an unstable, white *substance*, probably a decomposition product. The action of hydrogen chloride on a mixture of acetone and an arylhydroxylamine leads to the formation of the hydrochloride of the basic transformation product of the latter. When boiled with hydriodic acid, N-arylacetoximes are hydrolysed, forming their components, the hydroxylamine being then reduced to the corresponding amine. As mesityl oxide condenses with phenylhydroxylamine, forming a *product*, m. p. 107°, and with benzylhydroxylamine, forming an *additive* compound, $C_{13}H_{19}O_2N$, m. p. 101—102°, the reaction of acetone with arylhydroxylamines cannot be preceded by condensation of the ketone. When heated with hydroxylamine hydrochloride and sodium hydrogen carbonate in alcoholic solution, the condensation product of acetone and phenylhydroxylamine yields a *product*, $(C_6H_{10}ON)_x$, m. p. 135°; similarly, the condensation product of acetone and p-tolylhydroxylamine yields a *substance*, m. p. 112°, having approximately the same composition. It is considered that the condensation products of acetone with arylhydroxylamines may be formed by condensation of 2 mols. of the primary additive compound and be represented by the formula  $\mathrm{O}<\begin{matrix}\mathrm{NR\cdot CMe_2}\\ \mathrm{NR\cdot CMe_2}\end{matrix}>\mathrm{O}$ or $\mathrm{O}<\begin{matrix}\mathrm{NR\cdot CMe_2}\\ \mathrm{CMe_2\cdot NR}\end{matrix}>\mathrm{O}$.

It is now found that the action of phenylhydroxylamine on ethyl acetoacetate leads to the formation of two isomeric *products*, $C_{22}H_{24}O_5N_2$, crystallising in white prisms, m. p. 120—121° and 136° respectively, which when treated with glacial acetic acid are transformed into a third *isomeride* crystallising in needles, m. p. 137°. A mixture of this with the isomeride, m. p. 136°, has m. p. 110°. When treated with bromine in alcoholic solution, the three isomerides form a mixture of *mono-* and *di-bromo*-derivatives, m. p. 166°. The constitution of the condensation products of phenylhydroxylamine and ethyl acetoacetate, which may be stereoisomerides, is discussed. It is probable that the three substances are formed by way of an intermediate product,

$OH\cdot NPh\cdot CMe(OH)\cdot CH_2\cdot CO\cdot CH_2\cdot C(OH)(NPh\cdot OH)\cdot CH_2\cdot CO_2Et$,

which may undergo further condensation in various directions.

The action of *p*-tolylhydroxylamine on ethyl acetoacetate leads to the formation of only the one product, m. p. 172°, which has probably the constitution



$C_6H_4Me\cdot N{<}\begin{matrix}CMe\\ \|\\ C\cdot CO_2Et\end{matrix}$.

With bromine in alcoholic solution, it yields a *bromo*-derivative, $C_{13}H_{14}O_2NBr$, m. p. 190°.

Diacetyl and benzylhydroxylamine form a white, crystalline *additive* compound, $C_{11}H_{15}O_3N$, m. p. 107·5°, which gradually decomposes to a brown, viscid oil, and is soluble in hot, but insoluble in cold, solvents; its formation may serve to characterise benzylhydroxylamine. With hydrogen chloride, phenylhydrazine, phenylcarbimide, and hydroxylamine, the additive compound gives the reactions of its components.

Phenylhydroxylamine forms two white, crystalline *additive* compounds with diacetyl: $C_4H_6O_2,C_6H_7ON$, m. p. 95°, and

$2C_4H_6O_2,C_6H_7ON$,

m. p. 105°; the constitution of the former is represented by the formula $OH\cdot NPh\cdot CMe(OH)\cdot COMe$, but that of the latter, although discussed, remains undecided.

In the absence of a solvent, diacetyl and *p*-tolylhydroxylamine form a white, crystalline *additive* compound, $2C_4H_6O_2,C_7H_9ON$, m. p. 106°, but in solution and cooled by ice an *isomeride*, m. p. 132°. Naphthylhydroxylamine and diacetyl combine with slight development of heat, forming a viscid *product*. When heated with dilute mineral acids, the additive compounds of diacetyl and arylhydroxylamines are decomposed quantitatively into their components.

Methyl ethyl diketone reacts with β-substituted hydroxylamines with slight development of heat, forming unstable *products*. Attempts to form additive compounds of benzyl methyl diketone and benzil with β-substituted hydroxylamines were unsuccessful. G. Y.

Compounds of α-Naphthylcarbimide with Amino-Acids. CARL NEUBERG and E. ROSENBERG (*Biochem. Zeitsch.*, 1907, 5, 456—460).—By shaking the alkaline solutions of amino-acids with α-naphthylcarbimide, the following compounds were obtained. With *l*-alanine, $C_{14}H_{14}O_3N_2$, m. p. 202°; with *d-iso*leucine, $C_{17}H_{20}O_3N_2$, m. p. 178°; with *l*-aspartic acid, $C_{15}H_{14}O_5N_2$, m. p. 115°; with *l*-asparagine, $C_{15}H_{15}O_4N_3$, m. p. 199°; with *d*-phenylalanine, $C_{20}H_{18}O_3N_2$, m. p. 155°; with tryptophan, $C_{22}H_{19}O_3N_3$, m. p. 159—160°; with *dl*-serine, $C_{14}H_{14}O_4N_2$, m. p. 192°; with δ-aminovaleric acid, $C_{16}H_{18}O_3N_2$, m. p. 195—196°; with *dl*-leucylglycine, $C_{19}H_{23}O_4N_3$, m. p. 186°. The yield is mostly 80—90%; α-naphthylcarbimide derivatives can be precipitated as the very stable silver or copper salts, and these can be estimated by ignition. G. B.

Analysis of Pine Tar. PETER KLASON, JOHN KÖHLER, and F. FRIEDEMANN (*Arkiv. Kem. Min. Geol.*, 1907, 2, No. 36, 1—31).—Methods and results of analysis of pine tars of various origins are given (compare Ström, Abstr., 1900, i, 577). T. H. P.

Red and White Isomeric Silver Salts of 2 : 4 : 6-Tribromophenol. HENRY A. TORREY and WILLIAM H. HUNTER (*Ber.*, 1907, 40, 4332—4335).—Three methods are described for the preparation of a colourless silver 2 : 4 : 6-tribromophenoxide, of which the best is the following. The freshly precipitated red silver salt is dissolved in a small quantity of concentrated ammonium hydroxide, the solution diluted, and nearly neutralised with dilute sulphuric acid. After further dilution, the solution is treated with a concentrated solution of silver nitrate, whereby the pure white silver salt is generally precipitated. The red and the white varieties yield the same ethyl ether, and behave alike towards ethyl or methyl iodide in the absence of a solvent, forming an amorphous substance, m. p. above 250° (decomp.), which does not contain iodine.

The authors propose the ordinary benzenoid formula for the white salt, and an ortho-quinonoid formula for the red, $O\colon C_6H_2Br_2\colon BrAg$.

C. S.

Aminophenolsulphonic and Aminocresolsulphonic Acids. II. 3-Nitro- and 3-Amino-*o*-cresolsulphonic Acids. GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4319—4322. Compare Abstr., 1906, i, 837). —3-*Nitro*-o-*cresol*-5-*sulphonic acid*, prepared by heating 3-nitro-*o*-cresol with twice the quantity of concentrated sulphuric acid, crystallises with $3H_2O$. The *sodium*, *potassium*, *barium*, *strontium*, and *calcium* salts are described; those of the type $NO_2 \cdot C_7H_7(OH) \cdot SO_3M$ are less coloured than those containing two equivalents of the metal. By reduction with hydrochloric acid and stannous chloride, the acid yields 3-*amino*-o-*cresol*-5-*sulphonic acid*, which crystallises in needles containing $\frac{1}{2}H_2O$, and gives a deep red coloration with ferric chloride.

C. S.

Aminophenolsulphonic and Aminocresolsulphonic Acids. III. 4-Nitro- and 4-Amino-*m*-cresol-6-sulphonic Acids. GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4322—4323).—4-Nitro-*m*-cresol and concentrated sulphuric acid at 70° yield, after four to six hours, 4-*nitro*-m-*cresol*-6-*sulphonic acid*, which crystallises in needles; the *disodium* salt, $NO_2 \cdot C_7H_7(ONa) \cdot SO_3Na,3H_2O$, forms orange-yellow prisms. By reduction, the acid yields the corresponding *amino*-acid. C. S.

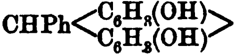
Aminophenolsulphonic and Aminocresolsulphonic Acids. IV. Sulphonation of 3-Nitro-*p*-cresol. GUSTAV SCHULTZ (*Ber.*, 1907, 40, 4324—4325).—3-Nitro-*p*-cresol is not attacked by concentrated sulphuric acid at the ordinary temperature, and is decomposed at higher temperatures. Fuming sulphuric acid at 0° converts it into an *acid*, $C_7H_8O_4$, m. p. 128°, which forms an *ethyl* ester, $C_6H_7O_2 \cdot CO_2Et$, b. p. 205°, with an odour of melons, of which the yellow *phenylhydrazone* has m. p. 96°, and the colourless *semicarbazone*, m. p. 110°. C. S.

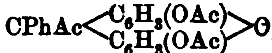
2-Amino-1-methylphenylene-4 : 5-dithiol [2-Amino-4 : 5-dithioltoluene] and Sulphineazo-dyes. FRITZ FICHTER, JAROSLAV FRÖHLICH, and MARX JALON (*Ber.*, 1907, 40, 4420—4425. Compare Fröhlich, this vol., i, 632).—In accordance with the views of Friedländer and Mauthner (Abstr., 1905, i, 102), the introduction of two mercaptan groups in positions ortho to one another into a simple azo-dye, such as *o*-tolueneazo-β-naphthylamine, is found to confer on the compound the characteristic dyeing properties of sulphur dyes.

2-Nitro-*p*-toluidine-5-sulphonic acid is converted by Leuckart's method (Abstr., 1890, 603) into *potassium* 4-*xantho*-2-*nitrotoluene*-5-*sulphonate*, $C_{10}H_{10}O_6NS_3K,1\frac{1}{2}H_2O$, obtained as very small, light brown, prismatic needles, decomposing above 150°. Hydrolysis by potassium hydroxide results in the formation of the *dipotassium* salt of 6-*nitro*-4-*thioltoluene*-3-*sulphonic acid*, $C_7H_5O_5NS_2K_2,2H_2O$, crystallising in brilliant, dark red prisms; a solution of the salt gives a light yellow precipitate with lead acetate. Both the solid salt and its aqueous solutions are oxidised by atmospheric oxygen to the *potassium* salt of the corresponding *disulphide*, $S_2[C_6H_2Me(NO_2)\cdot SO_3K]_2,5H_2O$, obtained as long, yellow needles, which is reduced by stannous chloride and hydrochloric acid to the corresponding *amine*, $S_2[C_6H_2Me(NH_2)\cdot SO_3H]_2$, forming small, colourless crystals. The potassium salt of the nitro-compound yields with phosphorus pentachloride the *sulphochloride*, $S_2[C_6H_2Me(NO_2)\cdot SO_2Cl]_2$, crystallising in light brown prisms, m. p. 208°, which on reduction is converted into 2-*amino*-4 : 5-*dithioltoluene*, the *hydrochloride* of which, $C_7H_9NS_2,HCl$, is obtained as a white, crystalline powder; the *lead* salt is orange-red; the *diethyl ether*, $C_{11}H_{17}NS_2$, is a thick oil, b. p. 225—227°/25 mm.; its *sulphate*, $(C_{11}H_{17}NS_2)_2,H_2SO_4$, crystallises in long, colourless, silky needles. 2-Amino-4 - 5-dithioltoluene is oxidised by the air with the formation of a *substance*, $(C_7H_7NS_2)_x$, obtained as an amorphous, yellow powder insoluble in the common solvents.

Toluene-2-azo-β-naphthylamine 4 - 5-*disulphide*, $C_{17}H_{13}N_3S_2$, obtained by the addition of β-naphthylamine to a diazotised solution of 2-amino-4 : 5-dithioltoluene as a dark red, amorphous powder, is insoluble in the common solvents, but dissolves in an aqueous alkali sulphide solution, forming a dark red solution which dyes unmordanted wool red. The precipitate obtained on acidifying this solution is partially soluble in alcohol, from which solution after a time, or on the addition of hydrogen peroxide, the disulphide separates; it is therefore probable that the disulphide is reduced to the dithiol before it dissolves. W. H. G.

Condensation of Aldehydes with Phenols. Condensation of Quinol with Benzaldehyde and Formaldehyde. Pawel Shorygin (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 1094—1109).—A short summary of the work done so far on the subject is given, and it is pointed out that one criterion for judging the mode of reaction of aldehydes and phenols in the cases which do not comply with the general rule has never been applied, namely, the determination of the molecular weights of the substances formed.

Quinol reacts with benzaldehyde, forming 3 : 6 : 3′ : 6′-*tetrahydroxytriphenylmethane*, $CHPh[C_6H_3(OH)_2]_2$, readily soluble in, but decomposed by, alkalis, dissolves in concentrated sulphuric acid, forming a dense, dark red liquid, reduces Fehling's solution, and when heated at ordinary or reduced pressure does not melt, but loses water and decomposes. Oxidising agents, such as chromic acid or hydrogen peroxide, also decompose it. When kept over phosphoric oxide, the *anhydride*,  $CHPh<\begin{smallmatrix}C_6H_3(OH)\\C_6H_3(OH)\end{smallmatrix}>O$, is formed, which, when exposed to air, is reconverted to the original compound.

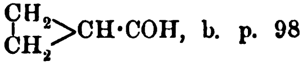
The *triacetyl* derivative, possibly  $CPhAc<\begin{smallmatrix}C_6H_3(OAc)\\C_6H_3(OAc)\end{smallmatrix}>O$, is hydrolysed readily, forming a brown, powdery *substance*, $C_{21}H_{16}O_4$, which decomposes on heating. The *tribenzoyl* derivative, $C_{40}H_{26}O_6$, is a light amorphous, pink powder, which turns dark red on heating and has m. p. 220—240° (decomp.).

With formaldehyde, quinol forms 3 : 6 : 3′ : 6′-*tetrahydroxydiphenylmethane*, $CH_2[C_6H_3(OH)_2]_2$, a light amorphous, brown powder, which decomposes on distillation at ordinary or reduced pressure, forming a small quantity of a colourless *substance*, m. p. 100—115°.

The diphenyl compound is very similar in properties to the triphenyl compound, but does not dissolve in sulphuric acid; with acetic anhydride, it forms a *diacetyl* derivative, $C_{17}H_{16}O_6$, a bright yellow, amorphous substance similar in properties to the corresponding triphenyl derivative. Z. K.

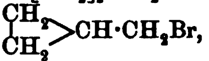
Main Constituent of Japanese Lac. RIKO MAJIMA and S. CHŌ (*Ber.*, 1907, **40**, 4390—4393. Compare Yoshida, Trans., 1883, **43**, 472; Tschirch and Stevan, Abstr., 1906, i, 31; Miyama, *japanische Amtsber.*, 1906, No. 1000).—Urushic acid has the composition C 79·65 and H 9·75 after careful purification by alcohol and petroleum; the "nitrogen" previously found in the acid was really carbon monoxide (Miyama, *loc. cit.*). Dry distillation of urushic acid gives methane, hexane, hexylene, heptane, heptylene, octane, octylene, $C_{14}H_{28}$, $C_{14}H_{26}$, and catechol, with small quantities of fatty acids and carbon dioxide. Oxidation with nitric acid gives a mixture from which oxalic, succinic, and suberic acids were isolated. Methylation of urushic acid gives a substance which has no longer phenolic reactions, is not hydrolysed by alcoholic potassium hydroxide, and not oxidised by nitric acid. Methoxyl determinations appear to show that about one-sixth of the oxygen is not methylated.

Urushic acid is readily acetylated and benzoylated, and these results show that urushic acid is a polyhydroxyphenol containing a large hydrocarbon grouping. W. R.

Preparation and Properties of Trimethylenecarbinol [*cyclo*-Propylcarbinol] and some of its Derivatives. NICOLAUS J. DEMJANOFF and K. FORTUNATOFF (*Ber.*, 1907, **40**, 4397—4399; *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1085—1094. Compare this vol., i, 1023).—Pure *cyclo*propylcarbinol was prepared by reducing ethyl *cyclo*propionate according to Bouveault and Blanc's method (Abstr., 1904, i, 642), and has b. p. 123·2—123·4°/738 mm., D_0^0 0·9154, $D_0^{17\cdot5}$ 0·8995, $n_D^{15\cdot1}$ 1·4313; the *urethane* forms needle-shaped crystals, m. p. 100—104°. With chromic acid, the alcohol yields the corresponding *aldehyde*,  $\begin{smallmatrix}CH_2\\|\\CH_2\end{smallmatrix}>CH\cdot COH$, b. p. 98°/734 mm., D_0^0 0·9473,

$D_0^{17\cdot6}$ 0·9294, $n_D^{15\cdot2}$ 1·4286, which yields a *semicarbazone*, m. p. 126°, soluble in ether.

Prolonged heating with hydrobromic acid causes the ring to break, and most of the alcohol is converted into a mixture of dibromides, mostly $CHMeBr\cdot CH_2\cdot CH_2Br$, together with $CH_2Me\cdot CHBr\cdot CH_2Br$ and $CH_2Br\cdot[CH_2]_2\cdot CH_2Br$. A small quantity of a *monobromide*, probably



$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!>\!CH\cdot CH_2Br$

, is also formed, and has b. p. 103°, n_D^{15} 1·4633, $D_0^{6\cdot8}$ 1·3740, D_0^{15} 1·3600. Z. K.

Fission of Substituted Phenyl Benzyl Ethers by Alkalis.

Karl Auwers [and, in part, Otto Mahler] (*Annalen*, 1907, **357**, 85—94. Compare Auwers and Rietz, this vol., i, 919).—Certain halogen substituted phenyl benzyl ethers (Auwers, Traun, and Welde, Abstr., 1900, i, 168) are hydrolysed, not only by strong acids, but also when gently heated with alcoholic alkalis, or even when boiled with acetic anhydride. As Kumpf (Abstr., 1884, 1005) and Frische (Abstr., 1884, 1337) found that di- and tri-nitro-derivatives of phenyl and *p*-tolyl benzyl ethers are hydrolysed by alcoholic potassium hydroxide, whereas the mono-nitro-derivatives and parent ethers remain unchanged, it seemed probable that the ease with which the halogen substituted ethers in question are hydrolysed depends on the accumulation of the negative substituting groups. The authors have now found that, when boiled with alcoholic potassium hydroxide for three days, mono- and di-bromo-, dichloro-, and bromonitro-derivatives of phenyl benzyl ether, as also tribromo-derivatives having the bromine atoms distributed between the two benzene nuclei, remain unchanged, whereas under the same conditions 2 : 4 : 6-tribromo-, pentabromo-, and 2 : 4 : 6-trichloro-phenyl, and 2 : 4 : 6-tri-iodo-*m*-tolyl benzyl ethers, as also 2 : 4-dichlorophenyl 4-nitrobenzyl ether, are completely hydrolysed to the phenol and benzyl alcohol in one day or less. Since *ψ*-cumyl and dibromo-*ψ*-cumyl benzyl ethers remain unchanged, the stability of phenyl benzyl ether is not diminished by the introduction of methyl groups.

The following substituted phenyl benzyl ethers are prepared by boiling the corresponding phenol with the benzyl chloride or bromide and sodium ethoxide in alcoholic solution.

o-*Bromophenyl benzyl ether*, $C_{13}H_{11}OBr$, slightly yellow oil, decomp. on distillation. p-*Bromophenyl benzyl ether*, $C_{13}H_{11}OBr$, rose-coloured needles, m. p. 64—65°. o-*Bromophenyl* o-*bromobenzyl ether*, $C_{13}H_{10}OBr_2$, viscid oil, which slowly crystallises, m. p. slightly above the ordinary temperature. p-*Bromophenyl* p-*bromobenzyl ether*, small, white needles, m. p. 111°. p-*Bromophenyl* o-*bromobenzyl ether*, oil, decomp. partially on distillation. o-*Bromophenyl* p-*bromobenzyl ether*, small, white needles, m. p. 72—74°. 2 : 4-*Dibromophenyl benzyl ether*, small needles, m. p. 68°. 2 : 4-*Dibromophenyl* o-*bromobenzyl ether*, $C_{13}H_9OBr_3$, long, white needles, m. p. 79°. 2 : 4-*Dibromophenyl* p-*bromobenzyl ether*, long, white needles, m. p. 93°. 2 : 4-Dichlorophenyl benzyl ether, $C_{13}H_{10}OCl_2$, crystallises in cubes, m. p. 61—62°. p-*Bromo-o-nitrophenyl benzyl ether*, $C_{13}H_{10}O_3NBr$, yellow needles, m. p. 84—85°. 2 : 4 : 6-*Tribromophenyl benzyl ether*, $C_{13}H_9OBr_3$, needles, m. p. 85°.

Pentabromophenyl benzyl ether, $C_{13}H_7OBr_5$, white needles, m. p. 203—204°. 2 : 4 : 6-*Trichlorophenyl benzyl ether*, $C_{13}H_9OCl_3$, long, white needles, m. p. 64—65°. *Tri-iodo*-m-*tolyl benzyl ether*, $C_{14}H_{11}OI_3$, white needles, m. p. 131°. 2 : 4-*Dichlorophenyl* p-*nitrobenzyl ether*, $C_{13}H_9O_3NCl_2$, yellow needles, m. p. 148—150°. *Benzyl ψ-cumyl ether*, $C_{16}H_{18}O$, prisms, m. p. 45°. *Benzyl dibromo-ψ-cumyl ether*, $C_{16}H_{16}OBr_2$, white needles, m. p. 110—111°. These ethers are readily or moderately soluble in organic solvents. G. Y.

Base-forming Property of Carbon. JAMES F. NORRIS (*Amer. Chem. J.*, 1907, **38**, 627—642).—Norris and Franklin (Abstr., 1903, i, 341) in discussing the properties of triphenylcarbinol suggested that by a change in the nature of the radicles, the basic property of the compound could be increased to such a degree that a true carbon base would be produced. The present investigation was undertaken with the object of studying this point.

When triphenylcarbinol is treated with cold hydrochloric acid (D 1·20), hydrobromic acid (D 1·49), or hydriodic acid (D 1·7), it is converted quantitatively into the corresponding triphenylmethyl halide.

Tri-*p*-tolylcarbinol has a greater basicity than the triphenyl-compound, and is converted into the chloride by hydrochloric acid of D 1·12. It reacts with nitric acid (D 1·42) with formation of the *nitrate*, $C(C_6H_4Me)_3 \cdot NO_3,2HNO_3$, whilst triphenylcarbinol is not affected by this treatment. Triphenylcarbinol dissolves in concentrated sulphuric acid, and is reprecipitated on the addition of a small quantity of water. The tritolyl-compound, however, dissolves in a mixture of equal volumes of sulphuric acid and water, and yields a *sulphate*, $C(C_6H_4Me)_3 \cdot HSO_4,H_2SO_4$, which forms deep orange-coloured, silky needles.

The compounds obtained from triphenylcarbinol behave as true salts. A solution of the chloride in acetone has electrical conductivity, and, when a direct current is passed through the solution, a red substance, probably analogous to triphenylmethyl, is deposited on the cathode. On adding silver nitrate to a solution of the chloride in acetone, silver chloride is precipitated. The chloride is decomposed by strong sulphuric acid with formation of the sulphate and liberation of hydrogen chloride. It reacts with alcohol, thus: $C(C_6H_4Me)_3Cl + EtOH \rightleftharpoons C(C_6H_4Me)_3 \cdot OEt + HCl$.

Benzyl alcohol can be converted into the chloride, bromide, and iodide by concentrated solutions of the halogen acids.

The behaviour of alcohols of the paraffin series under the same conditions has been studied. *tert.*-Butyl alcohol, when treated with concentrated hydrochloric acid, gives a quantitative yield of the chloride at the ordinary temperature. Usually, however, it is necessary to employ heat to bring about the reaction between alcohols and acids, and for this reason the mixtures of acids and water of constant boiling point have been used. In this way, yields of 91% and 89% were obtained of *tert.*-butyl bromide and iodide respectively, and 95% of *sec.*-butyl iodide.

When *sec.*-butyl alcohol was distilled with concentrated hydrochloric acid, the chloride was not produced, but, on using the acid of constant boiling point, a yield of 50% was obtained. The primary alcohols are not converted into the chlorides when distilled with hydrochloric acid.

This method is recommended for the preparation of alkyl bromides and iodides. On slowly distilling a mixture of the alcohol with a large excess of the acid of contant b. p., the halide passes over and collects in the early fractions. The product is shaken with concentrated hydrochloric acid to remove unchanged alcohol, and is afterwards dried and distilled. Excellent yields of methyl, ethyl, *n*- and *iso*-propyl, *iso*-, *sec*.-, and *tert*.-butyl, *iso*amyl, and allyl bromides and iodides have been obtained in this way. E. G.

A Vinyl Alcohol of the Type CArR:CH·OH. Marc Tiffeneau and Daufresne (*Compt. rend.*, 1907, **145**, 628—631).—The alcohol obtained from estragole dibromide by the successive action of alcoholic potassium acetate and potassium hydroxide is *β-anisyl-β-methylvinyl alcohol*, $OMe\cdot C_6H_4\cdot CMe{:}CH\cdot OH$, and not anisyl*cyclo*propanol as previously described (this vol., i, 515). This alcohol, b. p. 154—155°/14 mm., is stable in neutral or alkaline medium, and is converted into *p*-methoxyhydratropaldehyde by distillation under ordinary pressure, by the action of dilute acids, or when preserved in a vacuum over sulphuric acid. The *methyl ether*, $OMe\cdot C_6H_4\cdot CMe{:}CH\cdot OMe$, b. p. 262—264°, D 1·073, $D_4^{15\cdot 7}$ 1·0615, is identical with the ether obtained by the action of yellow mercuric oxide on the methyliodohydrin of anethole (Tiffeneau, this vol., i, 922); the *acetyl* derivative has b. p. 164—165°/13 mm., or 288° under ordinary pressure, D 1·123, $D_4^{16\cdot 8}$ 1·111, $n_D^{16\cdot 8}$ 1·5409. M. A. W.

The Solubility of Castor Oil in Lipoids. Wilhelm Filehne (*Beitr. Chem. Physiol. Path.*, 1907, **10**, 299—311).—The solubility of the lipoid, cholesteryl stearate, in olive oil, oleic acid, castor oil, ricinoleic acid, ψ-ricinoleic and crotonoleic acids has been determined by the methods of (1) melting point, (2) specific gravity, and (3) iodine value. Similarly, the solubilities of the oils and acids in the lipoid have been determined. J. J. S.

A Phytosterol from Echinophora spinosa. J. Tarbouriech and J. Hardy (*Chem. Zentr.*, 1907, ii, 969—970; from *Bull. Sci. Pharm.*, 1907, **14**, 387—392).—The fatty substances obtained from the roots of *Echinophora spinosa* yield on hydrolysis a *phytosterol* crystallising in small, white, orthorhombic plates, m. p. 148°. The following derivatives were prepared: *benzoate*, m. p. 145°; *acetate*, pearly-white leaflets, m. p. 124—125°; *propionate*, crystallising from alcohol in leaflets, m. p. 109—110°, but when precipitated by alcohol from a carbon tetrachloride solution, m. p. 105°. W. H. G.

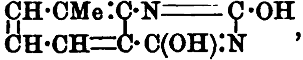
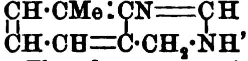
Production of Phenolic Acids by Oxidation of Ammonium Salts of Benzoic Acid. Henry D. Dakin and Mary Dows Herter (*J. Biol. Chem.*, 1907, **3**, 419—434).—Hydrogen peroxide, acting on the ammonium salts of benzoic acid or its chloro-, bromo-, nitro-, and amino-derivatives, can introduce hydroxyl groups into the nucleus, but the yield of phenolic acid is small. Hippuric acid undergoes nuclear oxidation with difficulty. Benzoic acid yields *o*-, *m*-, and *p*-hydroxybenzoic acids in about equal amount; on further oxidation, the last two yield protocatechuic (3 : 4-dihydroxybenzoic) acid, whilst salicylic acid yields 2:3-dihydroxybenzoic acid. Thus the second hydroxy-group takes up a position ortho to that already in the ring. A part of the benzoic acid is oxidised to carbon dioxide, and probably other products are also formed. The reaction occurs in approximately neutral solutions, and to some extent at the ordinary temperature. The possible origin of phenolic substances in animal and vegetable tissues is considered, and, although there is ample proof of their origin by the oxidation of preformed aromatic substances, there is little evidence at present that they originate directly from the condensation or rearrangement of aliphatic substances. W. D. H.

m-Toluic Acid. VICTOR JÜRGENS (*Ber.*, 1907, 40, 4409—4415).—It has been shown by Findeklee (Abstr., 1906, i, 42) and Kusel (Abstr., 1904, i, 619) that phthalylglycine esters containing a methyl or ethoxy-radicle in position 4, undergo the same transformation as phthalylglycine ester, being converted by sodium methoxide into *iso*quinoline derivatives (compare Gabriel and Colman, Abstr., 1905, i, 944). In order to see if phthalylglycine esters substituted in position 3 undergo a similar change, 3-*methylphthalylglycine ethyl ester* has been prepared and its behaviour towards sodium methoxide investigated; it is found to undergo no such transformation.

Several of the following new compounds were obtained in unsuccessful attempts to prepare 3-methylphthalic acid (compare Young, Abstr., 1892, 1221); the acid was finally obtained from methyl 2-nitro-*m*-toluate (compare Findeklee, Abstr., 1906, i, 21) by reduction to the amine, replacement of the amino-group by the cyano-group, and subsequent hydrolysis of the cyano-derivative.

2-Nitro-*m*-toluic acid, when treated with phosphorus pentachloride and subsequently with ammonia, is converted into the *amide*, $NO_2 \cdot C_6H_3Me \cdot CO \cdot NH_2$ [2 : 1 : 3], m. p. 192°; this compound when heated with phosphoric oxide yields 2-*nitro*-m-*toluonitrile*, $NO_2 \cdot C_6H_3Me \cdot CN$, crystallising in needles, m. p. 84°. The action of alcoholic ammonium sulphide on the latter compound leads to the formation of 2-*amino*-m-*toluamide*, $NH_2 \cdot C_6H_3Me \cdot CO \cdot NH_2$, m. p. 149°.

Methyl 2-*nitro*-m-*toluate*, $NO_2 \cdot C_6H_3Me \cdot CO_2Me$, m. p. 74°, yields, on reduction with tin and hydrochloric acid, the crystalline *hydrochloride* of *methyl* 2-*amino*-m-*toluate*, $C_9H_{11}O_2N,HCl,2H_2O$; the free *base* is a viscid oil with an odour like orange-peel. It is converted on diazotisation and treatment with cuprous cyanide into *methyl* 2-*cyano*-m-*toluate*, $CN \cdot C_6H_3Me \cdot CO_2Me$, crystallising in long, white, pointed needles, m. p. 68—70°. This compound is hydrolysed by hydrochloric acid to 3-methylphthalic acid; the *imide*, m. p. 187°, and anhydride, m. p. 114—115° (Young gives m. p. 109—110°), were prepared. 3-*Methylphthalylglycine*, $C_8H_3MeO_2{:}N \cdot CH_2 \cdot CO_2H$, resulting from the interaction of glycine and 3-methylphthalic anhydride, crystallises in white, felted needles, m. p. 195°; the *methyl* ester, m. p. 105°, as stated already, undergoes no transformation when treated with sodium methoxide.

2-*Amino*-m-*toluic acid*, m. p. 172°, the methyl ester of which is described above, reacts with potassium cyanate, forming 2 : 4-*dihydroxy*-8-*methylquinazoline*,  $\begin{array}{l}\mathrm{CH{\cdot}CMe{:}C{\cdot}N{=\!=}C{\cdot}OH}\\ \|\qquad\qquad |\qquad\quad |\\ \mathrm{CH{\cdot}CH{=}C{\cdot}C(OH){:}N}\end{array}$, a crystalline substance, m. p. 283°. It is converted by phosphorus pentachloride into 2 : 4-*dichloro*-8-*methylquinazoline*, $C_9H_6N_2Cl_2$, crystallising in fine, white, felted flakes, m. p. 140°. The latter compound is reduced by hydriodic acid to 8-*methyldihydroquinazoline*,  $\begin{array}{l}\mathrm{CH{\cdot}CMe{:}CN{=\!=}CH}\\ \|\qquad\qquad |\qquad\ |\\ \mathrm{CH{\cdot}CH{=}C{\cdot}CH_2{\cdot}NH}\end{array}$, short, pointed, prismatic crystals, m. p. 112°. The *chromate*, *aurichloride*, and *platinichloride*, $(C_9H_9N_2)_2,H_2PtCl_6$, are well-defined, crystalline substances. W. H. G.

Synthesis of Polypeptides. XXII. Derivatives of *l*-Phenylalanine. Emil Fischer and Walter Schoeller (*Annalen*, 1907, **357**, 1—24).—Polypeptides derived from optically active phenylalanine have not been prepared previously because of the difficulty of obtaining the active amino-acids. *r*-Phenylalanine has now been resolved into its active components by means of the formyl derivative (compare Fischer and Warburg, Abstr., 1906, i, 72). Whilst glycyl-*l*-phenyl alanine is obtained by the action of chloroacetyl chloride on *l*-phenylalanine, *l*-phenylalanylglycine is prepared by the action of ammonia on *d*-*a*-bromohydrocinnamoylglycine, which is formed from *d*-phenylalanine by way of *d*-*a*-bromohydrocinnamic acid (Fischer and Carl, this vol., i, 9) and *d*-*a*-bromohydrocinnamoyl chloride. These two dipeptides yield the same anhydride.

Formyl-r-*phenylalanine*, $C_{10}H_{11}O_3N$, prepared by heating *r*-phenylalanine with formic acid on the water-bath, crystallises from water in microscopic plates, softening at 165·5° (corr.), m. p. 168·8—169·8° (corr.); when heated with brucine and methyl alcohol, it dissolves and the solution on cooling deposits the *brucine* salt of the *d*-compound, which, on hydrolysis, yields *formyl*-d-*phenylalanine*, $[a]_D^{20}$ $-75·43°$ ($\pm 0·2°$). The *brucine* salt of the *l*-compound, obtained from the methyl alcohol filtrate, yields *formyl*-l-*phenylalanine*, $[a]_D^{20}$ $+75·2°$ ($\pm 0·2°$). The optically active formylphenylalanines crystallise from water in plates, soften at 163° (corr.), m. p. 167° (corr.), and are slightly more soluble than the *r*-compound. The optically active phenylalanines are prepared by boiling the formyl derivatives with *N*-hydrobromic acid and treatment of the resulting hydrobromides with ammonia. *d*-Phenylalanine prepared in this manner has m. p. 283° (corr.) (decomp.), $[a]_D^{20}$ $+35·14°$ ($\pm 0·5°$) (Fischer and Mouneyrat, Abstr., 1900, i, 647), and has a sweet taste. *l*-Phenylalanine, m. p. 283° (corr.) (decomp.), $[a]_D$ $-35·09°$ ($\pm 0·5°$) ($[a]_D^{16}$ $-38·1°$ to $-40·2°$; Schulze and Winterstein, *Zeitsch. physiol. Chem.*, 1902, **35**, 299), has a bitter taste, and when heated with formic acid yields the formyl derivative, $[a]_D^{20}$ $+72·4°$.

d-*a*-Bromohydrocinnamic acid, prepared by the action of nitric oxide on *d*-phenylalanine hydrobromide in hydrobromic acid in presence of bromine at $-10°$, or in a more impure state by the action of sodium nitrite on *d*-phenylalanine hydrobromide in 25% hydrobromic acid solution cooled by ice, has $[\alpha]^{20}_{D}$ $+9°$, and contains therefore about 13% of its optical isomeride. In the same manner, *l*-leucine hydrobromide on treatment with sodium nitrite in 49% hydrobromic acid solution yields *l*-α-bromo*iso*hexoic acid containing about 22% of the *d*-acid.

l-*Phenylalanine ethyl ester hydrochloride*, prepared by the action of hydrogen chloride on *l*-phenylalanine in alcoholic solution, crystallises in long, colourless needles, $[\alpha]^{20}_{D}$ $-7{\cdot}6°$ $(\pm 0{\cdot}2°)$. On treatment with hydrobromic acid and bromine, the l-*ester* forms a dark red oil, and on treatment with nitric oxide in cooled hydrobromic acid solution yields impure *ethyl* d-*α-bromohydrocinnamate*, b. p. 110°/0·35 mm., $[\alpha]^{20}_{D}$ $+20°$. *Ethyl* l-*α-bromohydrocinnamate*, prepared by esterification of a specimen of the *l*-acid containing 18% of the *d*-acid, has $[\alpha]_{D}$ $-15{\cdot}5°$. Hence the pure *l*-acid has $[\alpha]_{D}$ about $-24°$, and Walden's transformation does not take place in the formation of ethyl α-bromohydrocinnamate by the action of bromine and nitric oxide on *l*-phenylalanine ethyl ester.

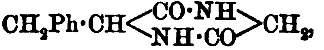
d-*α-Bromo-β-phenylpropionyl chloride*, prepared in an 85% yield from *d*-α-bromohydrocinnamic acid, $[\alpha]^{20}_{D}$ $+9°$, is obtained as a colourless oil, b. p. 90°/0·25 mm., has a suffocating odour, and contains at least 25% of the *r*-compound. d-*α-Bromo-β-phenylpropionylglycine*,

$$CH_2Ph{\cdot}CHBr{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

obtained by the action of the chloride and sodium hydroxide on glycine and extraction of the product with ether, crystallises on addition of light petroleum to the ethereal solution in long needles, m. p. 145—146° (corr.), $[\alpha]^{20}_{D}$ $-14{\cdot}65°$ $(\pm 0{\cdot}3°)$. The portion of the product insoluble in ether is the *r*-compound. On treatment with aqueous ammonia, the *d*-compound yields l-*phenylalanylglycine*, $CH_2Ph{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, which crystallises in needles, commences to sinter at about 219° (corr.), m. p. 224° (corr.) (decomp.), $[\alpha]^{20}_{D}$ $+54{\cdot}20°$ $(\pm 0{\cdot}4°)$, or after precipitation by addition of alcohol to the aqueous solution and drying at 80° over phosphoric oxide in a vacuum, $[\alpha]^{20}_{D}$ $+53{\cdot}63°$ $(\pm 0{\cdot}4°)$, and has a bitter taste; the aqueous solution has a slight acid reaction, and when boiling dissolves copper oxide, becoming blue.

Chloroacetyl-l-*phenylalanine*, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH(CH_2Ph){\cdot}CO_2H$, softens at about 123° (corr.), m. p. 126° (corr.), $[\alpha]^{20}_{D}$ $+51{\cdot}25°$ $(\pm 0{\cdot}5°)$, or after recrystallisation from water, $[\alpha]^{20}_{D}$ $+51{\cdot}80°$ $(\pm 0{\cdot}5°)$.

Glycyl-l-*phenylalanine*, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CH_2Ph){\cdot}CO_2H$, crystallises in colourless needles, m. p. 267° (corr.) (decomp.), $[\alpha]^{20}_{D}$ $+41{\cdot}4°$ $(\pm 0{\cdot}5°)$, or after recrystallisation from water, $[\alpha]^{20}_{D}$ $+42{\cdot}0°$ $(\pm 0{\cdot}5°)$, has a bitter taste, forms a slightly acid aqueous solution, and yields a blue solution when boiled with water and copper oxide; the *copper* salt forms an amorphous, blue mass. The *anhydride*,



$$CH_2Ph{\cdot}CH{<}{\begin{matrix}CO{\cdot}NH\\NH{\cdot}CO\end{matrix}}{>}CH_2,$$

formed from *l*-phenylalanylglycine or glycyl-*l*-phenylalanine by conversion into the methyl ester and treatment of this with alcoholic ammonia, crystallises in needles, m. p. about 265·5° (corr.) (decomp.),

$[\alpha]_D^{20}$ +100·5° (±0·4°), or after recrystallisation from water, $[\alpha]_D^{20}$ +99·5° (±0·5°). G. Y.

The Liberation of Carbon Monoxide from the Simplest Tertiary Acids, Trimethylacetic [αα-Dimethylpropionic] and Phenyldimethylacetic [α-Phenyl-α-methylpropionic] Acids. AUGUSTIN BISTRZYCKI and LOUIS MAURON (*Ber.*, 1907, 40, 4370—4378. Compare Abstr., 1901, i, 701; 1904, i, 44, 315; 1905, i, 285; 1906, i, 135).—It has been shown already that triphenylacetic acid, on dissolution in sulphuric acid, gives triphenylcarbinol, and carbon monoxide is eliminated quantitatively. On treating methyldiarylacetic acids similarly, carbon monoxide is again liberated quantitatively, but in these cases no carbinol is formed, the corresponding diaryloletine being obtained. The investigation has been extended to phenyldimethyl- and trimethyl-acetic acids. In these cases also, carbon monoxide is evolved quantitatively, but neither olefine nor carbinol is obtained. The elimination of carbon monoxide proceeds with most ease, and is most complete, in the case of tertiary acids, and least readily with monobasic primary acids, the secondary acids occupying an intermediary position.

α-Phenyl-α-methylpropionic acid (m. p. 80—81°; Wallach, *Nach. Wiss. Göttingen*, 1899, 126, gives 77—78°), on dissolution in sulphuric acid and heating for thirty minutes at 60—70° after being kept for thirty hours, yields, on neutralisation of the aqueous solution with barium carbonate, the *barium* salt of polymerised (?) *α-methylstyrenesulphonic acid*, $[(C_9H_9\cdot SO_3)_2Ba,6H_2O]_x$, crystallising in microscopic prisms; the *potassium* salt, $(C_9H_9O_3SK,H_2O)_x$, forms slender, silky needles. It is only very slowly hydrolysed by acids, and is therefore not an ester of sulphuric acid, and is supposed to be a polymeride of

$$SO_3H\cdot C_6H_4\cdot CMe{:}CH_2.$$

αα-Dimethylpropionic acid, when heated with sulphuric acid at 105—110° for three to four hours, yields iso*butylenedisulphonic acid*, $C_4H_6(SO_3H)_2$, in 35% yield as *potassium* salt, $C_4H_6O_6S_2K_2$, crystallising in leaflets. The *ammonium* salt, $C_4H_6O_6S_2(NH_4)_2$, forms plates, decomp. 248—251°; *lead* salt, $C_4H_6O_6S_2Pb,2H_2O$, large, rectangular plates. The acid itself, prepared from the lead salt, forms hexagonal plates, m. p. 63—64°, and is not hydrolysed. Further, it behaves like an unsaturated substance towards bromine water and potassium permanganate. It may have either of the four possible formulæ: $CH_2{:}C(CH_2\cdot SO_3H)_2$, $SO_3H\cdot CH{:}CMe\cdot CH_2\cdot SO_3H$, $CMe_2{:}C(SO_3H)_2$, $CH_2{:}CMe\cdot CH(SO_3H)_2$. W. R.

General Reaction for Differentiating between Multiple Linkings in Unsaturated Compounds of the Aromatic and Aliphatic Series. ETTORE MOLINARI (*Ber.*, 1907, 40, 4154—4161).—Ozone is quantitatively absorbed by compounds containing double linkings in the proportion of 1 mol. of ozone for each double linking, ozonides being formed; compounds, on the other hand, containing triple linkings do not absorb ozone. With benzenoid derivatives, where in the ring there is no "true" double linking, no ozone is absorbed; with those benzenoid derivatives which contain a "true" double linking, ozone is absorbed.

The behaviour of ozone towards stearolic acid, phenylpropiolic acid, and *o*-nitrophenylpropiolic acid was studied.

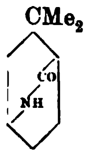
With aromatic compounds, the author draws the conclusion that, if a given substance does not take up ozone, the centric formula should be assigned to the compound in question; if ozone is absorbed, then the compound contains "true" double linkings. The following compounds absorb much ozone: resorcinol, quinol, phloroglucinol, pyrogallol, *p*-benzoquinone, cinnamic acid, phenanthrene, anthracene, hydrazobenzene, aminoazobenzene, benzidine, naphthalene, *a*-naphthylamine, *β*-naphthylamine, and quinoline. The following compounds do not absorb ozone: benzene, toluene, the xylenes, nitrobenzene, phenetole, hydrocinnamic acid, phenylpropiolic acid, *o*-nitrophenylpropiolic acid, diphenyl, benzophenone, diphenylmethane, fluorene, phenanthraquinone, azobenzene, naphthaquinone, anthraquinone, pyridine, and *iso*quinoline. Phenol and catechol absorb small quantities.

From the behaviour of benzene with ozone, the author concludes that the centric formula should be assigned to it, since benzene and ozone scarcely interact; this is opposed to the experience of Harries.

A. McK.

Esters of Hydroaromatic Amino-carboxylic Acids. ALADAR SKITA (*Ber.*, 1907, **40**, 4167—4182).—The object of this investigation was to ascertain if the substances are similar to the aliphatic amino-esters, to study *cis*- and *trans*-isomerism, and also to see if the property of local anæsthesia, possessed by ethyl aromatic *p*-amino-carboxylates, was characteristic of similar hydroaromatic compounds.

The compounds examined were all 4-aminocarboxylates. Ethyl *iso*phoronecarboxylate (ethyl 2 : 6 : 6-trimethyl*cyclo*-Δ^2-hexene-4-one-1-carboxylate) was prepared by the patented method (D.R.-P. 148080. Compare also Abstr., 1905, i, 349). When left in a methyl-alcoholic solution of hydroxylamine hydrochloride for eight days, and the solvent then distilled, *ethyl oximino*iso*phoronecarboxylate hydrochloride* is obtained in needles, m. p. 125°. The sodium salt of the oxime is hydrolysed by water; the *oxime*, $C_{12}H_{19}O_3N,\frac{1}{2}H_2O$, crystallises from dilute alcohol in slender needles, m. p. 78°. The oxime behaves differently towards various reducing agents. With sodium amalgam in alcohol, a 46% yield of *ethyl* cis-4-*amino*-2 : 6 : 6-*trimethyl*cyclo*hexane*-1-*carboxylate*, $C_{12}H_{23}O_2N$, is obtained as an oil, b. p. 124—125°/8 mm. (There is also a small fraction, b. p. 118—120°/9 mm., and 15% of the crude oil remains behind.) The *platinichloride*, $C_{24}H_{48}O_4N_2Cl_6Pt$, decomp. 248°; the *hydrogen citrate*, $C_{30}H_{54}O_{11}N_2$, forms hygroscopic crystals; the normal *citrate*, $C_{42}H_{77}O_{18}N_3$, is very hygroscopic. When the ester is boiled with sodium ethoxide for four hours and the alcohol removed, a *lactam*, $C_{10}H_{15}ON$, is obtained, crystallising from acetone in needles, m. p. 138—139°, b. p. 159—160°/9 mm. Not only have the elements of alcohol been lost, but two hydrogen atoms as well. This lactam formation shows the compound to be the *cis*-compound and to have the annexed grouping. Ethyl *iso*phoronecarboxylate and ammonium formate, when heated in a sealed tube at 200° for five hours, give



the formate of the amino-ester, and this on hydrolysis with 30% sulphuric acid yields the *cis*-modification.

Ethyl *iso*phoronecarboxylate, when treated with six times the theoretical amount of sodium amalgam in alcohol and acetic acid, gives an oil, which on fractional distillation is separated into two main fractions: (1) b. p. 127—130°/9 mm., solidifies on cooling; (2) b. p. 130—133°, and does not solidify. Both have the composition, $C_{12}H_{20}O_3$, of *ethyl dihydro*iso*phoronecarboxylates*; the two forms are probably derived from the ethylenic linkings becoming reduced.

The *oxime* of ethyl dihydro*iso*phoronecarboxylate (b. p. 148—150°/ 9 mm.) on reduction with sodium amalgam or with ammonium formate gives the *cis*-modification.

Ethyl trans-4-*amino*-2 : 6 : 6-*trimethyl*cyclo*hexane*-1-*carboxylate*, $C_{12}H_{23}O_2N$, obtained by the reduction of ethyl oximino*iso*phoronecarboxylate with sodium and alcohol, is an oil, b. p. 127—128°/11 mm., and is unchanged by twelve hours' boiling with sodium ethoxide solution. The *hydrochloride*, $C_{12}H_{24}O_2NCl$; *tartrate*, $C_{28}H_{52}O_{11}N_2$, and *platinichloride*, $C_{24}H_{48}O_4N_2Cl_6Pt$, decomp. 279°, have been prepared.

Another fraction, b. p. 150—160°/11 mm., obtained during the above reduction consists of a *bimolecular ethyl aminotrimethyl*cyclo*hexanecarboxylate*, $C_{24}H_{44}O_4N_2$, and the solid ethyl dihydro*iso*phoronecarboxylate has also been isolated.

By the reduction of the ethyl oximino*iso*phoronecarboxylate with sodium and methyl alcohol, a *lactimide-carboxylate*, $C_{10}H_{17}O_3N$, is obtained, crystallising from acetone in slender, white needles, m. p. 153—154°, b. p. 125°/8 mm. Hydroxylamine is not liberated from it by the action of hydrochloric acid.

Ethyl 4-*hydroxy*-2 : 6 : 6-*trimethyl*cyclo*hexane*-1-*carboxylate*, $C_{12}H_{22}O_3$, obtained by the action of nitrous acid on the corresponding amino-compound, is an oil, b. p. 144—148°/12 mm. Another substance obtained is ethyl *cyclo*geraniolenecarboxylate, $C_{12}H_{20}O_2$, b. p. 87—88°/ 8 mm., due to removal of the elements of water (D.R.-P. 148080).

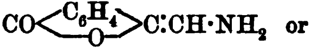
The *oxime hydrochloride* of ethyl dimethyl*cyclo*hexenonecarboxylate, $C_{11}H_{18}O_3NCl$, has m. p. 115°; the oxime itself is oily. Its reduction by sodium amalgam and acetic acid in the presence of sodium ethoxide yields the corresponding *amino*-ester, $C_{11}H_{21}O_2N$, an oil, b. p. 118—121°/ 8 mm., which has been characterised by preparing the *platinichloride*, $C_{22}H_{44}O_4N_2Cl_6Pt$, decomp. 250°, and the *citrate*, $C_{39}H_{71}O_{18}N_3$. This ester is a *cis*-form, because with sodium ethoxide it gives an oil, b. p. 156—158°/10 mm., which is apparently a lactam or mixture of lactams.

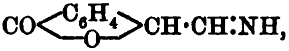
A physiological examination of the tartrates and citrates show them to be analogous to the aromatic amino-acids in possessing the property of local anæsthesia. W. R.

Preparation of Glyceryl Salicylate. CARL SORGER (D.R.-P. 186111).—Glyceryl monosalicylate, $C_3H_5(OH)_2 \cdot O \cdot CO \cdot C_6H_4 \cdot OH$, is readily obtained by heating methyl or ethyl salicylate with glycerol containing a trace of sodium hydroxide or some salt of sodium; the temperature is gradually raised to 220° and maintained until methyl or ethyl alcohol ceases to distil off. The glyceryl ester crystallises from ether in white needles. G. T. M.

Barium *p*-Hydroxybenzoate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1907, 711—713. Compare this vol., i, 532).—This salt dissolves easily in water, and the specific gravities of a number of solutions of different strengths are tabulated in the original. Unlike calcium *p*-hydroxybenzoate, it does not exhibit triboluminescence. The calcium salt dissolves easily in alcohol (95°), but the barium salt is soluble with difficulty in this solvent, and the solution becomes turbid on standing, depositing a mixture of the anhydrous and monohydrated salts. A solution of calcium *p*-hydroxybenzoate in alcohol, on the contrary, remains clear indefinitely.

Barium *p*-hydroxybenzoate does not dissolve in, and is not appreciably acted on by, either ethyl formate or acetate. T. A. H.

ω-Bromoacetophenone-*o*-carboxylic Acid. SIEGMUND GABRIEL (*Ber.*, 1907, 40, 4227—4239. Compare this vol., i, 214).—*Aminomethylenephthalide*,  $CO{<}\genfrac{}{}{0pt}{}{C_6H_4}{O}{>}C{:}CH\cdot NH_2$ or

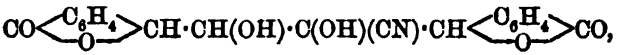


$$CO{<}\genfrac{}{}{0pt}{}{C_6H_4}{O}{>}CH\cdot CH{:}NH,$$

prepared by the action of ammonia on methyl ω-bromoacetophenone-*o*-carboxylate in presence of alcohol, crystallises from alcohol in yellow, quadratic leaflets, m. p. 176—178°, and is transformed into the oxime, m. p. 154—155°, of hydroxymethylenephthalide (*loc. cit.*) by the action of hydroxylamine. When treated with concentrated hydrochloric acid at 0°, aminomethylenephthalide is converted into hydroxymethylenephthalide and an isomeric *amino*-compound, $C_9H_7O_2N$, which separates from alcohol in oblong plates, sintering at 200°, m. p. 207°, and is also obtained by the action of aqueous ammonia on ω-bromoacetophenone-*o*-carboxylic acid.

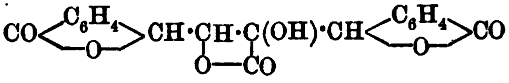
ω-Aminoacetophenone-o-carboxylamide, $NH_2\cdot CO\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2$, obtained by the action of aqueous ammonia on methyl ω-bromoacetophenone-*o*-carboxylate, separates from acetone in glistening crystals resembling whetstone, m. p. 144—145° (decomp.), is soluble in water, forms a crystalline *hydrochloride*, *hydrobromide*, and *picrate* (m. p. 214—215°), but yields no precipitate with auric or platinic chloride. In the same reaction is formed a *compound*, $(C_9H_5ON)_x$, which crystallises from aniline in bundles of orange-red, flat needles, m. p. 415° (decomp.).

To the compound, $C_9H_{13}O_6N$, m. p. 223°, formed by the action of potassium cyanide on ω-bromoacetophenone-*o*-carboxylic acid (*loc. cit.*) the author ascribes the constitution :



$$CO{<}\genfrac{}{}{0pt}{}{C_6H_4}{O}{>}CH\cdot CH(OH)\cdot C(OH)(CN)\cdot CH{<}\genfrac{}{}{0pt}{}{C_6H_4}{O}{>}CO,$$

which is supported by the following transformations. When treated with dilute sodium hydroxide solution, it yields hydrogen cyanide and hydroxymethylenephthalide.



$\mathrm{CO}\langle{}^{C_6H_4}_{\;O}\rangle\mathrm{CH}\cdot\underset{\mathrm{O{-}CO}}{\mathrm{CH}\cdot\mathrm{C}}(\mathrm{OH})\cdot\mathrm{CH}\langle{}^{C_6H_4}_{\;O}\rangle\mathrm{CO}$

When treated with cold concentrated hydrochloric acid or heated with 50% acetic acid, it is converted into the *trilactone*, which separates in oblique-ended prisms or six-sided plates, m. p. 245°, and reduces Fehling's solution when dissolved in alkali.

The action of dilute potassium hydroxide solution on this trilactone, followed by the addition of excess of hydrochloric acid, yields: (1) the *a-lactonic acid*, $C_{19}H_{14}O_8$, which crystallises in oblique-ended prisms, sintering at 190°, m. p. 199—200°; this lactonic acid is formed by the opening of one of the two end lactonic rings, and, when heated with acetic acid, yields a lactone, separating in colourless, cubical crystals, m. p. 191—194°, which is isomeric with the trilactone, m. p. 245°, and is termed the iso*lactone*; the a-lactonic acid yields a sparingly soluble *ammonium* salt, $C_{19}H_{13}O_8\cdot NH_4$, m. p. 188°, and a still less soluble *barium* salt; (2) the *β-lactonic acid*, $C_{19}H_{14}O_8$, separating as a crystalline powder, which froths at 180°, forming a pale yellow, turbid mass which becomes clear at 190°; it is readily soluble in water or alcohol, and, when treated with glacial acetic acid, loses water, giving the trilactone, m. p. 245°; the *silver* salt, $C_{19}H_{13}O_8Ag$, of the β-lactonic acid was prepared.

When the trilactone, m. p. 245°, is treated with an excess of cold barium hydroxide solution and the solution subsequently acidified with hydrochloric acid, it yields the a-lactonic acid and an isomeric *γ-lactonic acid*, $C_{19}H_{14}O_8,1\frac{1}{2}H_2O$, m. p. varying from 188—189° to 190—195°, according to the rapidity of heating; this γ-acid forms a crystalline *silver* salt, $C_{19}H_{13}O_8Ag$, and is converted by concentrated acetic acid into the original trilactone, m. p. 245°. When the latter is shaken in a closed flask with about three equivalents of dilute barium hydroxide, it yields the *barium* salt, $(C_{19}H_{15}O_{10})_2Ba_3$, of the tribasic acid,

$$CO_2H\cdot C_6H_4\cdot CH(OH)\cdot CH(OH)\cdot C(OH)(CO_2H)\cdot CH(OH)\cdot C_6H_4\cdot CO_2H,$$

which could, however, not be obtained in the free state, the barium salt giving the β-lactonic acid when treated with dilute sulphuric acid.

When heated with dilute barium hydroxide solution, the trilactone, m. p. 245°, is converted into formic and phthalidecarboxylic acids (*loc. cit.*), m. p. 152°, which, together with the compound,

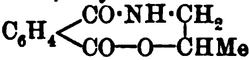
$$CO_2H\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot OH,$$

are the expected products of the tribasic acid referred to above.

When heated with phosphorus pentachloride, the trilactone loses water, yielding the *compound*, $C_{19}H_{10}O_6$, which crystallises from acetic acid in colourless, quadratic or oblong plates, sintering at 240°, m. p. 261—263°; the constitution of this compound is to be investigated.

T. H. P.

Derivatives of Imides of Dibasic Acids. PAUL MENDELSSOHN BARTHOLDY (*Ber.*, 1907, 40, 4400—4408).—The transformation of β-bromopropylphthalimide into the β-hydroxy-compound is shown to take place through the same intermediate stages as in the case of the isomeric γ-compound (compare Gabriel, Abstr., 1905, i, 649).

β-Bromopropylphthalamic acid, $C_3H_6Br\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, prepared by the action of alcoholic potassium hydroxide on β-bromopropylphthimide, crystallises in rhombic plates, m. p. 126°. The *imino-base*,  $C_6H_4<\begin{matrix}CO\cdot NH\cdot CH_2\\ CO-O-CHMe\end{matrix}$, obtained in the form of its *hydrochloride*, $C_{11}H_{11}O_3N,HCl$, deliquescent, white needles, m. p. 134—135°, by the action of dilute hydrochloric acid on the corresponding nitrosoamine (compare Gabriel, Abstr., 1905, i, 950), crystallises in rectangular prisms, m. p. 138°; the *platinichloride*,

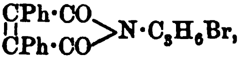
$$(C_{11}H_{11}O_3N)_2,H_2PtCl_6,2H_2O,$$

forms brilliant, golden, rhombic crystals, m. p. 190° (decomp.). The imino-base decomposes when its aqueous solution is heated, with the formation of *β-aminopropyl hydrogen phthalate*,

$$NH_2\cdot C_3H_6\cdot O\cdot CO\cdot C_6H_4\cdot CO_2H,$$

crystallising in rhombic plates, m. p. 168° (decomp.); the *hydrochloride*, $C_{11}H_{13}O_4N,HCl,2H_2O$, crystallises in pointed needles, melts partially at 87°, and is completely molten at 165°; the *platinichloride*, $(C_{11}H_{13}O_4N)_2,H_2PtCl_6,2H_2O$, forms large, prismatic needles, m. p. 204° (decomp.). *β-Hydroxypropylphthalimide*, $C_6H_4(CO)_2N\cdot C_3H_6\cdot OH$, results when β-bromopropylphthalimide is boiled with alcoholic potassium hydroxide; it crystallises in long prisms, m. p. 73°. *β-Bromoethylsuccinimide*, $C_4H_4O_2{:}N\cdot CH_2\cdot CH_2Br$, prepared by the action of ethylene bromide on sodium succinimide, forms white needles, m. p. 56—57°. It is converted by cold potassium hydroxide solution and subsequent treatment with hydrobromic acid into *β-bromoethylsuccinamic acid*, $C_2H_4Br\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, crystallising in leaflets, m. p. 101°. This substance is very unstable, and does not give a nitrosoamine when treated with potassium nitrite.

γ-Bromopropylsuccinimide, $C_4H_4O_2{:}N\cdot C_3H_6Br$, forms brilliant leaflets, m. p. 52°; the corresponding succinamic acid could not be obtained. An attempt to prepare β-bromopropylsuccinimide by the action of hydrogen bromide on allylsuccinimide was unsuccessful.

γ-Bromopropyldiphenylmaleinimide,  $\begin{matrix}CPh\cdot CO\\ \Vert\\ CPh\cdot CO\end{matrix}>N\cdot C_3H_6Br$, resulting from the interaction of sodium diphenylmaleinimide and trimethylene bromide, crystallises in broad, yellow needles, m. p. 112°. *β-Bromoethyldiphenylmaleinimide*, $C_4O_2Ph_2{:}N\cdot C_2H_4Br$, forms small, yellow crystals, m. p. 94°. These two derivatives of diphenylmaleinimide are more stable than the analogous phthalimide derivatives towards potassium hydroxide and hydrobromic acid.

Unlike phthalyl glycine ester, neither succinylglycine ester nor diphenylmaleylglycine ester is converted by sodium ethoxide into an *iso*quinoline derivative. *Diphenylmaleylglycine ester*,

$$C_4O_2Ph_2{:}N\cdot CH_2\cdot CO_2Et,$$

prepared by the action of ethyl chloroacetate on sodium diphenylmaleinimide, crystallises in yellowish-green needles, m. p. 109°. W. H. G.

Intramolecular Condensation of Phthalanilic Acid and of Certain Allied Compounds. II. J. Bishop Tingle and B. F. Lovelace (*Amer. Chem. J.*, 1907, 38, 642—652).—Tingle and Cram (this vol., i, 692) found that succinanilic acid readily combines with aniline to form the anilide, whilst phthalanilic acid in presence of aniline and alcohol is converted into phthalanil even at the ordinary temperature. It is now shown that the latter change is due to the intermediate formation of aniline phthalanilate, which easily loses water and aniline with production of the anil. It has been found that pyridine and quinoline react with the acid in a similar manner to give a quantitative yield of the anil.

β-Naphthylphthalamic acid reacts with aniline at 100° with formation of a mixture of phthalanil and β-naphthylphthalimide. Pyridine and quinoline under similar conditions give a quantitative yield of β-naphthylphthalimide. By the action of β-naphthylamine on the acid at 100°, a *compound* (probably di-β-naphthylphthalamide), m. p. 250° (decomp.), is obtained. Benzylamine similarly yields *dibenzylphthalamide*, $C_6H_4(CO{\cdot}NH{\cdot}CH_2Ph)_2$, m. p. 178—179°.

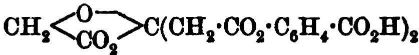
When benzylphthalamic acid is heated with aniline at 65°, benzylphthalimide is produced together with a small quantity of a substance, m. p. 177°, which is probably dibenzylphthalamide. Pyridine and quinoline react with the acid at 100° with formation of a quantitative yield of benzylphthalimide. Similarly, β-naphthylamine appears to give β-naphthylphthalimide. Benzylamine reacts with the acid at 65° or 100° with formation of dibenzylphthalamide. E. G.

2 : 4-(3 : 5-)Dihydroxytritanolactone and *m*-Hydroxytritanolactone. Hans von Liebig (*J. pr. Chem.*, 1907, [ii], **76**, 367—368). —The substance described as *m*-hydroxytritane (this vol., i, 930) is now found to be identical with Baeyer and Diehl's *o*-hydroxytriphenylmethane (this vol., i, 759), and therefore is *o*-hydroxytritane. It follows that the substance previously termed 3 : 5- is 2 : 4-dihydroxytritanolactone and that described as the 2 : 4- is the 2 : 6-dihydroxy-compound (Abstr., 1905, i, 781).

o-Hydroxytritane is formed when *o*-methoxytritane is boiled with concentrated hydriodic acid and glacial acetic acid. G. Y.

Anomalies in the Condensation of Benzilic Acid with Homologues of Benzene. Augustin Bistrzycki and Louis Mauron (*Ber.*, 1907, **40**, 4060—4065).—Benzilic acid in the presence of stannic chloride reacts in different ways with benzene and its monoalkyl homologues. Benzene and toluene yield the corresponding triarylated acetic acid; cumene reacts very slightly, the main product being diphenylacetic acid. This acid is also the main product of the reaction with ethylbenzene or propylbenzene in the presence of excess of benzene. *Ethyltriphenylacetic acid*, $C_6H_4Et{\cdot}CPh_2{\cdot}CO_2H$, m. p. 212—213°, is obtained when benzilic acid, stannic chloride, and ethylbenzene are heated for two to three hours; it crystallises from dilute alcohol in aggregates of colourless leaflets, and loses carbon monoxide quantitatively by treatment with concentrated sulphuric acid (Abstr., 1904, i, 315). p-*Propyltriphenylacetic acid*, m. p. 256—257°, behaves in a similar manner, forming p-*propyltriphenylcarbinol*, m. p. 153—155°.
C. S.

Preparation of Methylenecitrylsalicylic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 185800).—*Methylene-*

citrylsalicylic acid,  $CH_2{<}\substack{O\\CO_2}{>}C(CH_2\cdot CO_2\cdot C_6H_4\cdot CO_2H)_2$, colourless crystals, m. p. 150—155°, is obtained by condensing methylenecitryl chloride with salicylic acid in the presence of an agent for taking up hydrogen chloride, such as dimethylaniline or quinoline. It is also produced by digesting in benzene equivalent amounts of dipotassium salicylate and methylenecitryl chloride. It is more beneficial as an antirheumatic than acetylsalicylic acid, and has the additional property of yielding formaldehyde when hydrolysed by the alkaline intestinal juices. G. T. M.

Preparation of *o*-Nitrobenzaldehyde. ARNOLD REISSERT (D.R.-P. 186881. Compare this vol., i, 908).—The processes formerly employed to convert *o*-nitrotoluene into *o*-nitrobenzaldehyde either do not give a complete oxidation or lead to the formation of *o*-nitrobenzoic acid. It has now been found that the dimercury derivative of *o*-nitrotoluene (*loc. cit.*) is readily oxidised by dilute nitric or nitrous acid to *o*-nitrobenzaldehyde. To bring about this change, the dimercury compound is boiled with a 10% aqueous solution of potassium nitrate while 20% sulphuric acid is slowly added; the *o*-nitrobenzaldehyde is extracted with benzene or ether. A similar result is obtained when 20% nitric acid, or an aqueous solution of sodium nitrite, is added to a boiling mixture of 10% sulphuric acid and the dimercury compound.

G. T. M.

***p*-Dimethylaminobenzaldehyde. VI.** FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, **40**, 4356—4361. Compare, Abstr., 1903, i, 37; 1904, i, 506; 1905, i, 190, 202; 1906, i, 575).—It has been shown previously that, when magnesium methyl iodide and *p*-dimethylaminobenzaldehyde interact in the usual manner, the product is dimethylaminophenyl methyl carbinol, $NMe_2\cdot C_6H_4\cdot CHMe\cdot OH$. When, however, this product was heated at 100° with an excess of the Grignard reagent according to Klages' method, the corresponding unsaturated hydrocarbon, $NMe_2\cdot C_6H_4\cdot CH{:}CH_2$, was not formed, but, in place of it, *p*-dimethylamino*iso*propylbenzene, $NMe_2\cdot C_6H_4\cdot CHMe_2$, was produced. That the latter compound has the constitution formerly assigned to it is, in the present paper, still further proved, since cumidine is formed from it by the elimination of two of the alkyl groups by the method of von Braun.

N-Dimethylcumidine (*p*-dimethylamino*iso*propylbenzene) was prepared as previously described; its *picrate* has m. p. 112°, and its *methiodide*, m. p. 165°.

p-iso*Propylphenylmethylcyanamide*, $CN\cdot NMe\cdot C_6H_4\cdot CHMe_2$, obtained by the action of cyanogen bromide on *N*-dimethylcumidine and subsequent elimination of methyl bromide, is a yellow oil, b. p. 165°/10 mm. When boiled with 30% sulphuric acid for ten minutes, it forms N-*methyl*-p-iso*propylaniline*-N-*carboxylamide*,

$$NH_2\cdot CO\cdot NMe\cdot C_6H_4\cdot CHMe_2,$$

which separates in rod-shaped crystals, m. p. 118°. When boiled for two to three hours with 30% sulphuric acid, the latter compound is converted into N-*methylcumidine*, $NHMe\cdot C_6H_4\cdot CHMe_2$, which is a colourless oil, b. p. 111—112°/11 mm.; its *hydrochloride* forms glistening crystals, m. p. 128°; its *platinichloride* has m. p. 192°; its *picrate* has m. p. 147°; its *benzoyl* derivative separates from light petroleum in prisms, m. p. 58°. When acted on by phosphorus pentachloride, the benzoyl derivative is presumably first converted into the compound $CPhCl_2 \cdot NMe \cdot C_6H_4 \cdot CHMe_2$, from which methyl chloride is eliminated with formation of the imide chloride, $CPhCl{:}N \cdot C_6H_4 \cdot CHMe_2$, which readily gives *N*-benzoylcumidine, $NHBz \cdot C_6H_4 \cdot CHMe_2$; the latter compound crystallises from alcohol in glassy, spear-shaped crystals, m. p. 162°, and not 114° as given by Louis. The *N*-benzoylcumidine obtained was hydrolysed by heating at 150° for twelve hours with concentrated hydrochloric acid, and the resulting benzoic acid and *p*-cumidine identified. A. McK.

p-Dimethylaminobenzaldehyde. VII. FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, **40**, 4361—4367. Compare preceding abstract).—When magnesium organic compounds react with *p*-dimethylaminobenzaldehyde, three different products may be obtained: (1) carbinols, according to the normal action; (2) unsaturated hydrocarbons, when the carbinols are distilled under diminished pressure; (3) compounds, where the aldehydic oxygen atom is displaced by two alkyl groups. The method of conducting the latter change is as follows. The aldehyde (1 mol.) is gradually added to the ethereal solution of magnesium alkyl bromide (4 mol.). After some time, the ether is removed by heating the mixture, first on the water-bath, and finally under diminished pressure. The resulting grey, viscid mass is then heated in an oil-bath for about eight hours at 110°, and the product manipulated in the customary manner. The action of various magnesium organic compounds on *p*-dimethylaminobenzaldehyde is described in the present paper.

p-*Dimethylaminophenylpropylcarbinol* [α-p-*dimethylaminophenylbutane-α-ol*], $NMe_2 \cdot C_6H_4 \cdot CH(OH) \cdot CH_2 \cdot CH_2Me$, obtained by the action of magnesium propyl bromide on *p*-dimethylaminobenzaldehyde under normal conditions, melts at 35°, but was not obtained quite pure, owing to its tendency to form the corresponding styrene derivative; its *methiodide* separates from a mixture of alcohol and ether in glistening leaflets, m. p. 161°. When distilled under diminished pressure, the preceding secondary alcohol forms α-p-*dimethylaminophenyl-Δ^α-butylene*, $NMe_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CH_2Me$, which boils at 275° under ordinary pressure, and has m. p. 25°; the *platinichloride* melts indefinitely at 140°; the *picrate* has m. p. 114·5°, and the *methiodide*, m. p. 212°.

α-p-*Dimethylaminophenyl-γ-methylbutane-α-ol*,

$$NMe_2 \cdot C_6H_4 \cdot CH(OH) \cdot CH_2 \cdot CHMe_2,$$

obtained by the action of magnesium *iso*butyl bromide on *p*-dimethylaminobenzaldehyde, separates from light petroleum in stellate needles, m. p. 77°; its *methiodide* has m. p. 150°.

α-p-*Dimethylaminophenyl-γ-methyl-Δ^α-butylene*,

$$NMe_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CHMe_2,$$

boils at 148—149°/15 mm., is a liquid at the ordinary temperature, but solidifies when immersed in a freezing mixture; its *picrate* has m. p. 137°, and its *platinichloride*, m. p. 154°.

α-p-*Dimethylaminophenyl-δ-methylpentane-α-ol*,

$NMe_2\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CHMe_2$,

obtained from magnesium *iso*amyl bromide and *p*-dimethylaminobenzaldehyde, has m. p. 48°, and forms the *methiodide*, m. p. 141°.

α-p-*Dimethylaminophenyl-δ-methyl-*Δ^{α}*-pentene*,

$NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot CH_2\cdot CHMe_2$,

is a yellow oil at the ordinary temperature, b. p. 164—166°/9 mm., but solidifies when immersed in a freezing mixture; its *picrate* has m. p. 111°; its *platinichloride*, m. p. 167°, and its methiodide, m. p. 180°.

α-p-*Dimethylaminophenyl-β-methylpropane-α-ol*,

$NMe_2\cdot C_6H_4\cdot CH(OH)\cdot CHMe_2$,

obtained from magnesium *iso*propyl bromide and *p*-dimethylaminobenzaldehyde, has m. p. 39°.

α-p-*Dimethylaminophenyl-β-methyl-*Δ^{α}*-propylene*,

$NMe_2\cdot C_6H_4\cdot CH{:}CMe_2$,

boils at 134—135°/11 mm., and has m. p. 37°; its *picrate* has m. p. 140°, and its *methiodide*, m. p. 170°.

α-p-*Dimethylaminophenyldi*iso*propylmethane* [γ-p-*dimethylaminophenyl-βδ-dimethylpentane*], $NMe_2\cdot C_6H_4\cdot CH(CHMe_2)_2$, obtained from magnesium *iso*propyl bromide and *p*-dimethylaminobenzaldehyde, has m. p. 268°; its *picrate* has m. p. 150°, and its *methiodide* m. p. 171°.

α-p-*Dimethylaminophenyldi*iso*amylmethane* [ε-p-*dimethylaminophenyl-βθ-dimethylnonane*], $NMe_2\cdot C_6H_4\cdot CH(CH_2\cdot CH_2\cdot CHMe_2)_2$, obtained from magnesium *iso*amyl bromide and *p*-dimethylaminobenzaldehyde, is a colourless oil, b. p. 184—185°/13 mm.; its *methiodide* has m. p. 175°. A. McK.

Action of Magnesium Organic Compounds on *p*-Dimethylaminocinnamaldehyde. FRANZ SACHS and WALTER WEIGERT (*Ber.*, 1907, **40**, 4368—4369. Compare preceding abstract).—The authors have studied the action of magnesium organic compounds on *p*-dimethylaminocinnamaldehyde. When magnesium ethyl bromide is used, the corresponding carbinol is not obtained, but the product, when distilled under diminished pressure, gives α-p-*dimethylaminophenyl-*$\Delta^{\alpha\gamma}$*-pentadiene*, $NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CHMe$, which separates from alcohol in yellow crystals, m. p. 65°. Its solution in concentrated sulphuric acid is brown, and in dilute sulphuric acid red; its *picrate* has m. p. 145°. γ-*Phenyl*-α-p-*dimethylaminophenyl-*Δ^{α}*-propene-γ-ol*(3), $NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot CHPh\cdot OH$, obtained from magnesium phenyl bromide and *p*-dimethylaminocinnamaldehyde, has m. p. 160° (decomp.); its ethereal solution is yellow; its solution in glacial acetic acid is red; its solutions in chloroform and alcohol respectively brown. δ-*Phenyl*-α-p-*dimethylaminophenyl-*$\Delta^{\alpha\gamma}$*-butadiene*,

$NMe_2\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CHPh$,

obtained from magnesium benzyl chloride and *p*-dimethylaminocinnamaldehyde, separates from light petroleum in yellow crystals, m. p. 171°. A. McK.

[Arylsulphonic Esters of Salicylaldehyde and its Homologues.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 185547).—The arylsulphonic esters of salicylaldehyde are produced by shaking together at 70° an arylsulphonyl chloride and the aqueous solution of the sodium derivative of salicylaldehyde. The p-*toluenesulphonyl* derivatives of salicyl-, *o*-homosalicyl-, and *p*-homosalicylaldehydes are well-defined crystalline compounds melting respectively at 52—60°, 62°, and 68—69°. *Benzenesulphonyl*-p-*homosalicylaldehyde*, m. p. 63°, crystallises from petroleum in rectangular plates. When these arylsulphonyl derivatives are heated with the alkylbenzylanilinesulphonic acids in the presence of aqueous acids, leucodisulphonic acids are produced, which, on oxidation with acetic acid and lead dioxide, give rise to coloured disulphonic acids of the malachite-green series. G. T. M.

Preparation of 4-Benzoylaminoaceto-1:2-dialkyloxybenzenes. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 185598).—The action of hippuryl chloride on catechol leads to the attachment of the hippuryl group to one of the hydroxylic oxygens, with the formation of monohippuryl catechol. When this condensation is effected in the presence of aluminium chloride with a 1:2-dialkyloxybenzene instead of catechol, the hippuryl group enters the ring in the para-position to one of the oxygen atoms, so that compounds having the general formula $C_6H_3(OR)_2\cdot CO\cdot CH_2\cdot NH\cdot COPh$ are produced, these substances being utilised in the preparation of physiologically active compounds. 4-*Benzoylaminoacetylveratrole*, $C_6H_3(OMe)_2\cdot CO\cdot CH_2\cdot NH\cdot COPh$, felted needles, m. p. 155°, and 4-benzoylaminoacetyl-1:2-diethoxybenzene, $C_6H_3(OEt)_2\cdot CO\cdot CH_2\cdot NH\cdot COPh$, needles, m. p. 162°, are thus obtained from veratrole and 1:2-diethoxybenzene respectively. G. T. M.

Hexahydroacetophenone, Dodecahydrobenzophenone, Dodecahydrodiphenyl, and other Hydroaromatic Derivatives. CARL HELL and OSCAR SCHAAL (*Ber.*, 4162—4166. Compare von Braun, this vol., i, 893).—The best method of preparation of *cyclo*hexyl methyl ketone is from *cyclo*hexanol by first preparing *cyclo*iodohexane, then causing the magnesium *cyclo*hexyl iodide to condense with acetaldehyde, and oxidising the secondary alcohol so obtained to the ketone. The yield is 50% of the *cyclo*hexanol employed. Contrary to von Braun's statement, this ketone gives a hydrogen sulphite compound. *cyclo*Hexyl methyl ketone is also obtained in small yield by the distillation of a mixture of barium *cyclo*hexanecarboxylate and acetate; acetone, and *di*cyclo*hexyl ketone*, $CO(C_6H_{11})_2$, an oily liquid, b. p. 158—161°/14 mm., are also formed. Attempts to prepare *cyclo*hexyl methyl ketone by reducing acetophenone by sodium and amyl alcohol, by the condensation of acetyl chloride and *cyclo*hexanol, and by the interaction of acetonitrile and magnesium *cyclo*hexyl iodide were without result.

The yield of iodo*cyclo*hexane from *cyclo*hexanol is quantitative, whereas that of the bromo- and chloro-derivatives is only 50% (compare Freundler and Dammond, Abstr., 1905, i, 890).

All three haloid compounds give by the Grignard reaction the normal organomagnesium compound, *cyclo*hexene, and, in addition, the iodide yields *dodecahydrodiphenyl* [*di*cyclo*hexyl*], $C_6H_{11}\cdot C_6H_{11}$, an agreeable-smelling liquid, m. p. 4°, b. p. 234°/760 mm. A cryoscopic determination shows the mol. wt. to be 164, calc. 166; it reacts in sunlight very energetically with bromine.

Magnesium methyl iodide and ethyl *cyclo*hexanecarboxylate give *cyclo*hexyldimethylcarbinol, b. p. 85—86°/14 mm. (compare Sabatier and Mailhe, Abstr., 1904, i, 810); the corresponding *diethyl* compound, $C_6H_{11}\cdot CEt_2\cdot OH$, has b. p. 104—106°/14 mm. The *diphenyl* compound is an oily liquid, which loses water at 210—220°/14 mm., and by several distillations the unsaturated *hydrocarbon*, $C_6H_{10}{:}CPh_2$, is obtained, crystallising from methyl alcohol in prisms, m. p. 84°. W. R.

Halogen Derivatives of Benzophenone and of Di- and Tri-phenylmethane. FRANS M. JAEGER (*Zeitsch. Kryst. Min.*, 1907, **44**, 50—60).—Determinations of the crystalline forms of the following compounds: 2-bromobenzophenone; 2 : 4′-dichlorobenzophenone; 2 : 4 : 6-trichlorobenzophenone; 4 : 4′-dichlorodiphenylmethane; α-4 : 4′-trichlorodiphenylmethane; α-bromodiphenylmethane; phenylindoxazen; 4 : 4′ : 4″-tribromotriphenylmethane; 4 : 4′ : 4″-trinitrotriphenylcarbinol; reduction product from 4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacolin; 4 : 4′ : 4″ : 4‴-tetrachlorotetraphenylethane.

L. J. S.

Reaction Between Unsaturated Compounds and Organic Magnesium Compounds. XII. Aldehydes and Ketones. ELMER P. KOHLER (*Amer. Chem. J.*, 1907, **38**, 511—561).—In an earlier paper (Abstr., 1904, i, 595), an account was given of the action of organic magnesium compounds on αβ-unsaturated ketones containing phenyl in combination with the carbonyl group. On comparing the reactions of these phenyl ketones with those of corresponding methyl ketones, it has been observed that in the latter αβ-addition takes place with formation of unsaturated alcohols, whilst, in the former, saturated ketones are produced by αδ-addition:

$$\text{I. } CHPh{:}CH\cdot COMe + MgRX = CHPh{:}CH\cdot CMeR\cdot OMgX \longrightarrow CHPh{:}CH\cdot CMeR\cdot OH.$$

$$\text{II. } CHPh{:}CH\cdot COPh + MgRX = CHPhR\cdot CH{:}CPh\cdot OMgX \longrightarrow CHPhR\cdot CH_2\cdot COPh.$$

An investigation has been made with the object of ascertaining whether all unsaturated ketones behave in one or other of these ways, or whether substances could be found which would give both reactions. It has been found that certain ketones react in both ways, but that the relative proportions in which the αβ- and αδ-addition takes place depend on the nature of the unsaturated compound, the number and arrangement of the hydrocarbon residues and the character of the magnesium derivative. Experiments have been made to determine the relative importance of these factors, and attempts have been made to estimate the amounts of the various products.

In carrying out the experiments, the unsaturated compound was added gradually to a large excess of the reagent, cooled in a freezing mixture. The product was poured on ice and treated with hydrochloric acid to remove basic salts. The ethereal layer was separated, dried, and distilled; the residue was dissolved in acetone and treated with powdered potassium permanganate, the temperature being kept below 20°. In this way, the unsaturated products were destroyed and the saturated ketone could be collected and weighed. The quantitative results are expressed as the percentage of the unsaturated compound represented by the amount of $\alpha\delta$-additive product obtained. Most ketones yield both unsaturated alcohols and saturated ketones, whilst aldehydes yield the former only.

It is shown that the activity of the carbonyl group in unsaturated ketones varies in the same way as that of the corresponding saturated compounds, and that it merely determines the rate of the reaction. The final result depends quite as much on the rate of $\alpha\delta$-addition, and substances in which the activity of the carbonyl group is approximately the same may give almost entirely different products with the same reagent. The reactivity of the unsaturated compounds undergoes a gradual diminution as the hydrogen atoms are successively replaced by hydrocarbon residues, and the phenomena observed can be satisfactorily explained as being due to steric hindrance. The effect produced on the reaction by the nature of the magnesium derivative is shown by the different relative amounts of $\alpha\beta$- and $\alpha\delta$-additive products obtained with magnesium ethyl and magnesium phenyl bromides. Variations in the temperature and solvent do not appreciably affect the result.

The behaviour of unsaturated compounds resembles that of tautomeric substances, but in the case of the unsaturated ketones the results cannot be explained by intermediate compounds or by assuming that only one of the products is formed directly. In this case, the two additive reactions are so independent of each other that their rates are governed by quite different factors. The only satisfactory explanation therefore is that these unsaturated compounds can exist in two modifications, such as $C{:}C{\cdot}O{:}C$ and $-C{\cdot}C{:}C{\cdot}C-$.

By the action of magnesium ethyl bromide on acraldehyde, ethylvinylcarbinol is produced, whilst with magnesium phenyl bromide, phenylallyl alcohol is formed.

Ethylideneacetone reacts with magnesium methyl bromide with formation of dimethyl*iso*allylcarbinol and methyl *iso*butyl ketone, the latter forming about 75% of the product. With magnesium ethyl bromide, ethylideneacetone yields 75% of *γ-methylhexane-ε-one*,

$$CHMeEt{\cdot}CH_2{\cdot}COMe,$$

b. p. 146—147°, whilst with magnesium phenyl bromide it gives 40% of *β-phenylpropyl methyl ketone*, $CHPhMe{\cdot}CH_2{\cdot}COMe$, b. p. 132°/22 mm., which furnishes an *oxime*, b. p. 160°/22 mm., as a viscous liquid.

In the case of mesityl oxide, $\alpha\delta$-addition does not take place.

Benzylideneacetone (styryl methyl ketone) reacts with magnesium ethyl bromide or iodide with production of 60% of *phenylhexanone*, $CHPhEt{\cdot}CH_2{\cdot}COMe$, b. p. 130°/18 mm., which yields an *oxime*, b. p. 170°/20 mm. With magnesium phenyl bromide, it gives 12% of *ββ-diphenylethyl methyl ketone*, $CHPh_2{\cdot}CH_2{\cdot}COMe$, b. p. 194°/20 mm.

(compare Abstr., 1904, i, 596). The *ketoxime* exists in two forms, m. p. 91° (plates) and 128° (needles).

Styryl ethyl ketone, on treatment with magnesium ethyl bromide, yields 71% of *γ-phenylheptanone*, $CHPhEt\cdot CH_2\cdot COEt$, b. p. 255°, which gives an *oxime*, b. p. 172°/18 mm. With magnesium *iso*butyl bromide, a similar yield of *δ-phenyl-γ-methyloctane-ζ-one*,

$$CHMeEt\cdot CHPh\cdot CH_2\cdot COEt,$$

b. p. 152°/17 mm., is obtained, which furnishes an *oxime*, b. p. 185°. With magnesium phenyl bromide, *αα-diphenylpentane-γ-one*,

$$CHPh_2\cdot CH_2\cdot COEt,$$

b. p. 334—335°, is produced in a yield of 40% of the unsaturated ketone; its *oxime* exists in two stereoisomeric modifications, m. p. 146° (needles) and 117° (plates).

Styryl *iso*propyl ketone reacts with magnesium ethyl bromide with formation of 100% of *γ-phenyl-ζ-methylheptane-ε-one*,

$$CHPhEt\cdot CH_2\cdot COPr^{\beta},$$

b. p. 138°/15 mm.; the *oxime* has b. p. 175°/18 mm. With magnesium phenyl bromide, 88% of *αα-diphenyl-δ-methylpentane-γ-one*,

$$CHPh_2\cdot CH_2\cdot CO\cdot CHMe_2,$$

m. p. 66°, is produced, which forms colourless prisms and yields two isomeric *oximes*, m. p. 151° (needles) and 99° (plates); the *β-bromo*-derivative, $CHPh_2\cdot CHBr\cdot CO\cdot Pr^{\beta}$, m. p. 108°, crystallises in needles, and is converted by potassium hydroxide into *αα-diphenyl-δ-methyl-*Δ^{α}*-pentene-γ-one*, $CPh_2{:}CH\cdot CO\cdot CHMe_2$, b. p. 210—211°/15 mm.

Benzylidenepinacoline, on treatment with magnesium ethyl bromide, yields 100% of *γ-phenyl-ζζ-dimethylheptane-ε-one*,

$$CHPhEt\cdot CH_2\cdot CO\cdot CMe_3,$$

b. p. 145°/15 mm., m. p. 34°, which crystallises in needles, and yields a mixture of *oximes*, m. p. 83° (needles) and 36° (prisms). With magnesium phenyl bromide, 100% of *αα-diphenyl-δδ-dimethylpentane-γ-one*, $CHPh_2\cdot CH_2\cdot CO\cdot CMe_3$, m. p. 85°, is obtained, and forms slender needles. If acetyl chloride is added to the magnesium compound produced by the action of magnesium phenyl bromide on benzylidenepinacoline, *αα-diphenyl-δδ-dimethyl-*Δ^{β}*-pentenyl γ-acetate*,

$$CHPh_2\cdot CH{:}C(CMe_3)\cdot OAc,$$

m. p. 165°, is obtained, and crystallises in brilliant plates. The magnesium compound does not react with simple alkyl halides, but reacts with diphenylbromomethane with formation of the *diphenylmethyl ether* of αα-diphenyl-δδ-dimethyl-Δ^{β}-pentene-γ-ol,

$$CHPh_2\cdot CH{:}C(CMe_3)\cdot O\cdot CHPh_2,$$

m. p. 224°, which crystallises in plates. *β-Bromc-αα-diphenyl-δδ-dimethylpentane-γ-one*, $CHPh_2\cdot CHBr\cdot CO\cdot CMe_3$, m. p. 145°, crystallises in plates, and is converted by potassium hydroxide into *αα-diphenyl-δδ-dimethyl-*Δ^{α}*-pentene-γ-one*, $CPh_2{:}CH\cdot CO\cdot CMe_3$, m. p. 66°, which forms pale yellow plates.

p-Methoxybenzylideneacetone reacts with magnesium ethyl bromide to form 63% of *γ-*p*-methoxyphenylhexane-ε-one*,

$$OMe\cdot C_6H_4\cdot CHEt\cdot CH_2\cdot COMe,$$

b. p. 170°/18 mm., which yields an *oxime*, b. p. 195°/18 mm.

Dibenzylideneacetone and magnesium ethyl bromide react with formation of 91% of *benzylidenephenylhexanone* [*αε-diphenyl-*Δ^{α}*-heptene-*

γ-one], $CHPh\colon CH\cdot CO\cdot CH_2\cdot CHPhEt$, b. p. 224—228°, m. p. 87°, which forms long needles; the *oxime*, m. p. 117°, crystallises in needles. With magnesium phenyl bromide, 73% of *benzylidenediphenylbutanone* [*αεε-triphenyl-Δ^{α}-pentene-γ-one*], $CHPh\colon CH\cdot CO\cdot CH_2\cdot CHPh_2$, m. p. 136°, is produced, which forms pale yellow needles, and yields an *oxime*, m. p. 144°, which crystallises in needles. By the action of bromine on the preceding compound, *αβ-dibromo-αεε-triphenylpentane-γ-one*,

$$CHPhBr\cdot CHBr\cdot CO\cdot CH_2\cdot CHPh_2,$$

is obtained, and forms colourless needles.

Diphenylheptenone reacts with magnesium ethyl bromide to form 100% of *γη-diphenylnonane-ε-one*, $CHPhEt\cdot CH_2\cdot CO\cdot CH_2\cdot CHPhEt$, m. p. 56°, which crystallises in needles. With magnesium phenyl bromide, 93% of *ααε-triphenylheptane-γ-one*,

$$CHPh_2\cdot CH_2\cdot CO\cdot CH_2\cdot CHPhEt,$$

m. p. 72°, is produced together with about 7% of an unsaturated compound formed by αβ-addition; the *bromo*-derivative,

$$CHPh_2\cdot CHBr\cdot CO\cdot CH_2\cdot CHPhEt,$$

m. p. 153°, crystallises in needles.

Triphenylpentenone and magnesium ethyl bromide yield 100% of triphenylheptanone. With magnesium phenyl bromide, 99% of tetraphenylpentanone is produced together with a very small proportion of unsaturated compounds formed by αβ-addition. *β-Bromo-ααεε-tetraphenylpentane-γ-one*, $CHPh_2\cdot CHBr\cdot CO\cdot CH_2\cdot CHPh_2$, m. p. 160°, crystallises in needles.

Trichloroethylideneacetophenone reacts with magnesium phenyl bromide with formation of 95% of *ααα-trichloro-β-phenylbutyrophenone*, $CCl_3\cdot CHPh\cdot CH_2\cdot COPh$, m. p. 137°.

Benzylideneacetophenone and magnesium ethyl bromide yield 99% of *β-phenylvalerophenone* [*γε-diphenylpentane-ε-one*],

$$CHPhEt\cdot CH_2\cdot COPh,$$

m. p. 63°, which forms thin needles and gives an *oxime*, m. p. 87°. With magnesium phenyl bromide, 94% of diphenylpropiophenone is produced.

Anisylideneacetophenone and magnesium ethyl bromide react with formation of 98% of p-*methoxyphenylvalerophenone*,

$$OMe\cdot C_6H_4\cdot CHEt\cdot CH_2\cdot COPh,$$

m. p. 58°, which crystallises in thick, lustrous needles; the *oxime*, m. p. 92°, forms prisms. With magnesium phenyl bromide, 96% of *anisylphenylpropiophenone*, $OMe\cdot C_6H_4\cdot CHPh\cdot CH_2\cdot COPh$, m. p. 93°, is produced and forms stout needles.

Anisyl styryl ketone and magnesium ethyl bromide yield 100% of *β-phenylbutyl anisyl ketone*, $CHPhEt\cdot CH_2\cdot CO\cdot C_6H_4Me$, m. p. 85°, which crystallises in long, thin needles, and furnishes an *oxime*, m. p. 72°. With magnesium phenyl bromide, 99% of *diphenylethyl anisyl ketone*, $CHPh_2\cdot CH_2\cdot CO\cdot C_6H_4\cdot OMe$, m. p. 118°, is produced; its *bromo*-derivative, m. p. 144°, is converted by potassium hydroxide into *β-phenylstyryl anisyl ketone*, $CPh_2\colon CH\cdot CO\cdot C_6H_4\cdot OMe$, m. p. 103°, which yields a *bromo*-derivative, $CPh_2\colon CBr\cdot CO\cdot C_6H_4\cdot OMe$, m. p. 157°.

Cinnamoylmesitylene, $CHPh\colon CH\cdot CO\cdot C_6H_2Me_3$, m. p. 63°, prepared by adding aluminium chloride to a solution of mesitylene and cinnamoyl chloride in carbon disulphide, forms large, yellow plates, and is converted by bromine into *αβ-dibromo-β-phenylpropionylmesitylene*, $CHPhBr\cdot CHBr\cdot CO\cdot C_6H_2Me_3$, m. p. 122° (decomp.). It reacts with magnesium phenyl bromide with formation of 100% of *ββ-diphenylpropionylmesitylene*, $CHPh_2\cdot CH_2\cdot CO\cdot C_6H_2Me_3$, which yields a *bromo*-derivative, $CHPh_2\cdot CHBr\cdot CO\cdot C_6H_2Me_3$, m. p. 172°. When the bromo-derivative is treated with potassium hydroxide, it is converted into *phenylcinnamoylmesitylene*, $CHPh_2{:}CH\cdot CO\cdot C_6H_2Me_3$, m. p. 104°, which forms dark yellow plates.

By the reactions of bromobenzylideneacetophenone, benzylidenepropiophenone, and benzylidenedeoxybenzoin with magnesium alkyl halides, unsaturated compounds formed by αβ-addition are not produced, and it is evident therefore that substituents in the α-position interfere with the addition to the carbonyl group.

Dypnone reacts with magnesium ethyl bromide with formation of 44% of *β-phenyl-β-methylvalerophenone*, $CPhMeEt\cdot CH_2\cdot COPh$, b. p. 202°/18 mm.; its *oxime*, b. p. 222°/15 mm., is amorphous. The quantity of diphenylbutyrophenone formed by the action of magnesium phenyl bromide on dypnone (Abstr., 1904, i, 596) is 41%.

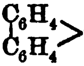
Phenylbenzylideneacetophenone and magnesium ethyl bromide yield 18% of *ββ-diphenylvalerophenone*, $CHPh_2Et\cdot CH_2\cdot COPh$, b. p. 252°/15 mm.; its *oxime* was prepared. With magnesium phenyl bromide, a saturated ketone is not produced, but the unsaturated alcohol and hydrocarbon are obtained, which have been described by Vorländer, Siebert, and Osterburg (Abstr., 1906, i, 346).

Diphenylbenzylideneacetophenone, $CPh_2{:}CPh\cdot COPh$, m. p. 153°, obtained by the action of potassium hydroxide on bromotriphenylpropiophenone, forms pale yellow needles and is very inactive. When treated with magnesium ethyl bromide, an unsaturated hydrocarbon is produced, and indications are obtained of the formation of a saturated ketone.

Magnesium phenyl bromide reacts with benzoylphenylacetylene with formation of hydroxytriphenylpropinene (benzophenonephenylacetylene) (Nef, Abstr., 1900, i, 21), but a saturated ketone is not produced.

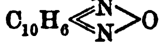
E. G.

Derivatives of Fluorenoneoxime. Contribution II. to the Theory of Colour. Julius Schmidt and Julius Söll (*Ber.*, 1907, 40, 4257—4260. Compare this vol., i, 630).—The authors have prepared fluorenone and its oxime and various derivatives of the latter, and have repeatedly crystallised them from suitable solvents until their colours underwent no further change. Thus purified, fluorenone is reddish-yellow; fluorenoneoxime, bright yellow; its sodium salt, pale yellow; its acetyl and benzoyl derivatives, bright yellow; and its methyl ether, reddish-yellow. As with phenanthraquinone, so also with fluorenone, replacement of the ketonic oxygen by the hydroxyimino-group is accompanied by brightening of the colour. Not so distinct, but still appreciable, is the effect which the introduction of acetyl, benzoyl, or sodium into the molecule of fluorenoneoxime has in brightening the colour.

Fluorenoneoxime methyl ether,  $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C:N\cdot OMe$, crystallises from alcohol in reddish-yellow needles, m. p. 145—146°, and dissolves readily in all the ordinary solvents except light petroleum.

The acetyl derivative of fluorenoneoxime has m. p. 79°; Wegerhoff (*Annalen*, 1888, **252**, 36; Abstr., 1889, 1066) gave 76°.

These derivatives of fluorenoneoxime are dissolved by concentrated sulphuric acid, giving reddish-brown solutions, from which they are precipitated by the addition of water. T. H. P.

Constitution and Colour of Derivatives of *o*-Benzoquinone- and Naphthaquinone-dioximes. Arthur Hantzsch and Walter H. Glover (*Ber.*, 1907, **40**, 4344—4350. Compare this vol., i, 101).—Whilst *o*-benzoquinonedioxime is faintly coloured, it forms dark red salts and also a colourless anhydride. It could not be determined whether the alkyl (or acyl) derivatives of the type $OR\cdot N:C_6H_4:N\cdot OR$ are colourless, since the salts are so readily transformed into the anhydrides, thus: $C_6H_4<\begin{matrix}N\cdot ONa\\N\cdot OH\end{matrix} = C_6H_4<\begin{matrix}N\\N\end{matrix}>O + NaOH$. Analogous derivatives of *β*-naphthaquinonedioxime, $OR\cdot N:C_{10}H_6:N\cdot OR$, are yellow, in spite of the fact that the anhydride,  $C_{10}H_6<\begin{matrix}N\\N\end{matrix}>O$, is colourless. The intensity of the colour of these compounds depends largely on the solvent. The dioxime salts of the benzene series are red, those of the phenanthrene series yellow; the alkyl and acyl derivatives of the naphthalene series are yellow, those of the phenanthrene series are colourless. The intensity of colour during salt formation from derivatives of *o*-benzoquinonedioxime indicates that the latter are *pseudo*-acids.

Aqueous solutions of *o*-benzoquinonedioxime are yellow and faintly acid in reaction. Determinations of electrical conductivity showed that *o*-benzoquinonedioxime is 100 times as weak as acetic acid. The solutions of the dioxime in alkalis are blood-red; the salts are, however, very unstable, and from their aqueous solutions the colourless anhydride separates. When dry ammonia is passed into the yellow solution of the dioxime in absolute ether, there is no precipitate, and the colour does not change. The solutions of the dioxime in strong acids are also blood-red. Tetrabromo-*o*-benzoquinonedioxime benzyl ether was not formed from benzyl hydroxylamine and tetrabromo-*o*-benzoquinone; in place of it, *benzylhydroxylaminotribromo-o-quinone*, $C_6Br_3O_2:NH\cdot O\cdot C_7H_7$, was produced; it separates from glacial acetic acid or benzene in orange-coloured needles, m. p. 170° (decomp.).

Various salts of *β*-naphthaquinonedioxime *a*-methyl ether were prepared, namely, the *normal potassium* salt, *hydrogen potassium* salt, and the *silver* salt. The *benzoyl* derivative, $OMe\cdot N:C_{10}H_6:N\cdot OBz$, has m. p. 116—119°; the yellow tint of the benzoyl derivative in various solvents is not so pronounced as that of the parent substance.

β-Naphthaquinonedioxime a-benzyl ether, $OH\cdot N:C_{10}H_6:N\cdot O\cdot C_7H_7$, obtained by the action of hydroxylamine on benzyl ether monoxime, separates from a mixture of chloroform and acetone in yellow prisms, m. p. 168°; its *benzoyl* derivative forms needles, m. p. 116°. The colour of these compounds in various solvents was studied.

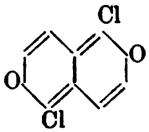
A. McK.

Quinonoid Compounds. XIV. *amphi*Naphthaquinones. II.

RICHARD WILLSTÄTTER and JAKOB PARNAS (*Ber.*, 1907, **40**, 3971—3979. Compare this vol., i, 425).—An account of the formation of 1 : 5-dichloro*amphi*naphthaquinone and its derivatives.

1 : 5-*Dichloro*-2 : 6-*dihydroxynaphthalene*, $C_{10}H_6O_2Cl_2$, prepared by the action of chlorine on 2 : 6-dihydroxynaphthalene in glacial acetic acid solution, crystallises in needles containing $2C_2H_4O_2$, lost on exposure to air, or from benzene in hexagonal plates, m. p. 223·5° (corr.), and forms a *diacetate*, $C_{14}H_{20}O_4Cl_2$, crystallising in plates, m. p. 179° (corr.).

1 : 5-*Dichloro*amphi*naphthaquinone* (annexed formula), obtained in a 36—45% yield by oxidation of the 2 : 6-dihydroxy-compound with lead dioxide in benzene solution, crystallises from chloroform in reddish-yellow prisms, or from alcohol in golden needles, or from benzene-light petroleum in brownish-yellow needles, m. p. 206·5° (corr.) (intumesces), is not volatile, odourless, stable in air, and more stable than *amphi*naphthaquinone towards organic solvents; it dissolves only slowly in alkalis, gives an olive-green coloration with concentrated sulphuric acid, and is reduced to 1 : 5-dichloro-2 : 6-dihydroxynaphthalene by sulphurous acid, dilute hydriodic acid, or phenylhydrazine in benzene solution. The dichloro*amphi*naphthaquinone is an energetic oxidising agent; it gives a blue coloration with guaiacum resin solution, converts hydrocoerulignone into coerulignone, and forms malachite-green from the *leuco*-base. It yields a colourless, crystalline *acetate* with acetic anhydride in presence of sulphuric acid, and combines with 2 : 6-dihydroxy- and 1 : 5-dichloro-2 : 6-dihydroxynaphthalenes, forming amphi*naphthaquinonehydrones*, crystallising in dark green needles, and giving an intense emerald-green coloration with concentrated sulphuric acid.



The action of *as*-benzoylphenylhydrazine on 1 : 5-dichloro*amphi*naphthaquinone in glacial acetic solution leads to the formation of the *a*-*benzoylphenylhydrazone* of 5-chloro-6-hydroxy-*β*-naphthaquinone, $C_{23}H_{15}O_3N_2Cl$, which crystallises in yellowish-red plates or red prisms, m. p. 224° (corr.), is extracted unchanged from its ethereal solution by dilute potassium hydroxide, is stable towards phenylhydrazine in boiling benzene solution, and forms a brilliant reddish-yellow solution in alcohol, which is decolorised by zinc dust and acetic acid. When treated with concentrated sulphuric acid, the benzoylhydrazone is hydrolysed, forming the *a*-*phenylhydrazone*, $C_{16}H_{11}O_2N_2Cl$, which crystallises from glacial acetic acid in yellowish-red needles, m. p. 198° (corr.), and dissolves in aqueous alkalis forming intense brownish-red, or in very dilute alkalis in bluish-red, solutions. The phenylhydrazone and benzoylphenylhydrazone on treatment with benzoyl chloride in pyridine solution yield the *dibenzoyl* derivative, $C_{30}H_{19}O_4N_2Cl$, which crystallises in brownish-yellow prisms, m. p. 208·5° (corr.), gives a cherry-red coloration with concentrated sulphuric acid, and forms benzanilide on reduction with zinc dust and acetic acid. G. Y.

Preparation of Leucohydroxyanthraquinone. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 183332).—Leucoquinizarin is produced from 2:4-dinitro-1-anthraquinone by reducing this to the corresponding diamino-compound with stannous chloride and then boiling the mixture for eight hours; the *leuco*-base separates on cooling. A similar result is obtained on reducing 2:4-dinitro-1-hydroxyanthraquinone with sodium sulphide and then boiling the 2:4-diamino-1-hydroxyanthraquinone thus produced with stannous chloride and hydrochloric acid.

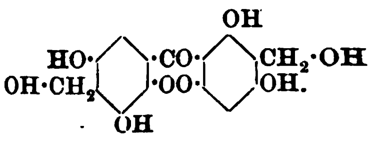
The reduction of the dinitrohydroxyanthraquinones containing one nitro-group in the ortho- and one in the para-position to the hydroxy-compound leads to the same result as the reduction of the mono-nitro-compounds, but, as the polynitro-derivatives are more readily obtained, there is a technical advantage in starting with the more highly nitrated products. G. T. M.

Preparation of Alkylated 4:8-Diaminoanthrarufins. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 185546).—Alkylated 4:8-diaminoanthrarufins are obtained by treating the 4:8-halogen derivatives of anthrarufin with the monoalkylamines in the presence of a catalyst, such as copper. The products when sulphonated furnished valuable wool dyes.

s-4:8-*Diethyldiaminoanthrarufin*, bronze needles, m. p. 292°, and s-4:8-*dimethyldiaminoanthrarufin*, dark blue needles, m. p. above 300°, were prepared by heating at 100° in the presence of copper powder 4:8-dibromoanthrarufin and 20% alcoholic solutions of ethylamine and methylamine respectively. G. T. M.

Preparation of 1:2:5-Trihydroxyanthraquinone and 1:2:5-Trihydroxyanthraquinone-3-sulphonic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 178631).—1:2:5-*Trihydroxyanthraquinone* is obtained readily by heating 5 parts of sodium alizarin-5-sulphonate with 15 parts of sodium hydroxide and 3 parts of water at 180—200°, and then acidifying the aqueous extract of the fused mass. The trihydroxy-compound is deposited in yellow flakes. The alkali fusion of sodium alizarin-3:5-disulphonate leads to the production of sodium 1:2:5-*trihydroxyanthraquinone*-3-*sulphonic acid*, which separates in yellow flakes, soluble in water, and reprecipitated by salting out. G. T. M.

Preparation of ω-Dihydroxydimethyl-2:6-anthrachrysone. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 184768).—Anthrachrysone readily reacts with formaldehyde in alkaline solution to yield an insoluble yellow condensation product, which is probably *ω-dihydr-*



oxydimethyl-2 : 6-*anthrachrysone*. The *sodium* salt is a well-defined, sparingly soluble compound, separating in garnet-red crystals.

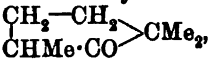
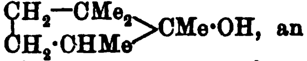
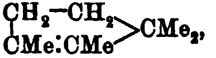
G. T. M.

Syntheses in the Camphor Group. Complete Synthesis of Campholene. GUSTAVE BLANC (*Compt. rend.*, 1907, **145**, 681—683).—The author has synthesised campholene by a similar method to that employed in the synthesis of its lower homologue, *iso*laurolene (Abstr., 1906, i, 523). *Ethyl β-methylpentane-βεε-tricarboxylate*,

$$CO_2Et\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2,$$

obtained by the condensation of ethyl γ-bromo-αα-dimethylbutyrate with ethyl sodiomalonate, is a colourless liquid, b. p. 175°/12 mm., and reacts with methyl iodide in the presence of sodium ethoxide to yield *ethyl β-methylhexane-βεε-tricarboxylate*,

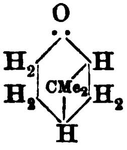
$$CO_2Et\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CMe(CO_2Et)_2,$$

b. p. 168°/14 mm.; the corresponding *acid* forms sparingly soluble, white needles, melts at 205°, losing carbon dioxide and forming *ααδ-trimethyladipic acid*, $CO_2H\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H$, m. p. 113—114°, which is probably identical with the acid obtained by Wallach and Kempe in the oxidation of pulenone (Abstr., 1904, i, 74). ααδ-Trimethyladipic anhydride is converted by careful distillation into 1 : 1 : 4-*trimethyl*cyclo*pentane*-5-*one*,  $\begin{array}{l}CH_2\text{—}CH_2\\ CHMe\cdot CO\end{array}\!\!>CMe_2$, b. p. 152°, a liquid having an odour similar to that of camphor or menthone; it forms an *oxime*, m. p. 62°, and condenses with magnesium methyl iodide to form the *tertiary alcohol*,  $\begin{array}{l}CH_2\text{—}CMe_2\\ CH_2\cdot CHMe\end{array}\!\!>CMe\cdot OH$, an oily liquid, b. p. 72°/18 mm., having an intense musty, camphoraceous odour, which yields campholene,  $\begin{array}{l}CH_2\text{—}CH_2\\ CMe{:}CMe\end{array}\!\!>CMe_2$, on distillation under ordinary pressure.

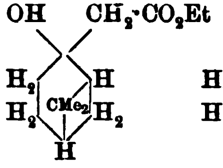
M. A. W.

Terpenes and Ethereal Oils. LXXXVIII. OTTO WALLACH (*Annalen*, 1907, **357**, 49—71).—I. *Synthesis from Nopinone of a Hydrocarbon related to β-Pinene.*—β-Pinene (nopinene) occurs commonly in small amounts in various turpentine oils, but, as it has not yet been isolated from these, its physical and other properties are not definitely known. It seemed therefore of interest to synthesise a hydrocarbon having the structure of β-pinene. Starting from nopinone (Wallach and Blumann, this vol., i, 936), this has now been accomplished by the method previously employed (Abstr., 1906, i, 563) for the introduction of a methylene group into cyclic hydrocarbons.

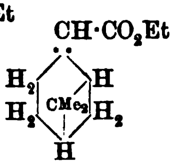
The action of zinc and ethyl bromoacetate on nopinone (I) in benzene solution leads to the formation of the *hydroxy*-ester (II), which has not been isolated, but when heated, after removal of the benzene, with potassium hydrogen sulphate at 150° yields the unsaturated *ester* (III). On hydrolysis of this, the *acid* is obtained as a syrup, b. p. 190—210°/13 mm.; the *silver* salt, $C_{11}H_{15}O_2Ag$, was analysed. When distilled under atmospheric pressure, the acid loses carbon dioxide and forms a *β-pinene* (IV), b. p. 158°, D^{20} 0·8630, $[\alpha]_D$ +15·93° undiluted, or +12·76° in ethereal solution, n_D^{20} 1·4699 :



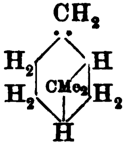
(I.)



(II.)



(III.)

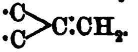


(IV.)

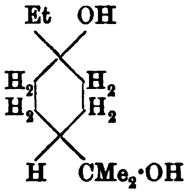
On oxidation with potassium permanganate and sodium hydroxide at 0°, the hydrocarbon yields a sparingly soluble *sodium* salt, which resembles sodium nopate obtained from turpentine oil, but is dextrorotatory; the *silver* salt, $C_{10}H_{15}O_3Ag$, was analysed. The *acid* crystallises from benzene in needles, m. p. 154—155°, is dextrorotatory, and differs from nopic acid in recrystallising unchanged from dilute sulphuric acid. The benzene mother liquors from the acid contain small amounts of a *substance*, m. p. 110—122°. Oxidation of the acid with permanganic acid leads to the formation of a *ketone*, $C_9H_{14}O$, m. p. about 60°, which yields a *semicarbazone*, $C_{10}H_{17}ON_3$, m. p. 206—207°.

The action of hydrogen chloride on the hydrocarbon leads to the formation of liquid *additive* compounds, whilst that of sulphuric acid leads to the formation of a crystalline, saturated, secondary *alcohol*, $C_{10}H_{17}\cdot OH$, which has an odour of camphor, and on oxidation with chromic acid yields a *ketone*, $C_{10}H_{16}O$. This solidifies below 0°, has an odour of camphor and menthone, and forms a *semicarbazone*, $C_{11}H_{19}ON_3$, crystallising in needles, m. p. 220—221° (compare Aschan, this vol., i, 630).

The relation of the synthetical β-pinene to that occurring in turpentine oil is discussed; it is considered that a change in the configuration takes place during the conversion of the nopinone into the synthetical hydrocarbon. Of special interest is the formation of a secondary alcohol from a hydrocarbon containing the grouping:

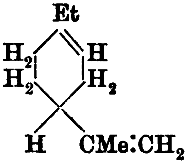

$\begin{matrix}\cdot C\\ \cdot C\end{matrix}\!\!>C{:}CH_2$.

II. *Synthesis of Homologous Compounds of the Dipentene Series.*—It has been shown (Wallach and Blumann, *loc. cit.*) that methylnopinol is readily converted, on the one hand, into terpin hydrate and dipentene, and, on the other, into terpinolene and terpinene. Probably optically active limonene and α-pinene also are formed. These reactions have now been employed in the formation of homologues of the terpene derivatives.



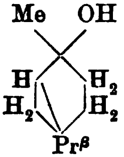
Ethylnopinol, $C_{11}H_{20}O$, prepared by the action of magnesium ethyl iodide on nopinone, forms large crystals, m. p. 43—45°, b. p. 219—223°, and when heated with formic acid loses water and yields homologous terpenes. When shaken with 5% sulphuric acid, ethylnopinol yields a *homologue* of terpin hydrate having the annexed constitution, which forms transparent crystals containing H_2O, m. p. 75—76°, and is readily converted into the *dihydrochloride*, $C_{11}H_{18},2HCl$, m. p. 63—64°. This is formed also by the action of hydrogen chloride on ethylnopinol in glacial acetic acid solution, and closely resembles dipentene dihydrochloride. The *dihydrobromide*, $C_{11}H_{18},2HBr$, m. p. 82—84°; the *dihydriodide*, m. p. 63—64°.

The *hydrocarbon*, $C_{11}H_{18}$, b. p. 201—202°, prepared by treating the dihydrochloride with aniline, yields a crystalline *tetrabromide*, $C_{11}H_{18}Br_4$, m. p. 124—125°, and a crystalline *nitrosochloride*, which loses hydrogen chloride, forming an *oxime*, converted by acids into an *oil* with an odour of carvone. The hydrocarbon is probably a homologue of dipentene having the annexed constitution, mixed with small amounts of an isomeride of the terpinolene series.



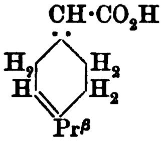
n-*Propylnopinol*, $C_{12}H_{22}O$, b. p. 225—235°, is formed in only small amount together with considerable quantities of nopinol by the action of magnesium *n*-propyl iodide on nopinone; it is converted by treatment with sulphuric acid into a *terpin*, which yields a crystalline *dihydrochloride*, $C_{12}H_{20},2HCl$.

III. *Synthesis in the Terpinene Series.*—*Methylsabinaketol* (*sabinene hydrate*), m. p. 38—39°, b. p. 195—201°, prepared by the action of magnesium methyl iodide on sabinaketone, has a terpineol odour, is stable towards permanganate, and on treatment with hydrogen bromide in glacial acetic acid solution yields terpinene dihydrochloride, m. p. 58—59°. When shaken with 5% sulphuric acid, sabinene hydrate yields terpineneterpin, m. p. 137° (this vol., i, 228).

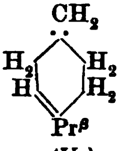


Ethylsabinaketol, $C_{11}H_{20}O$, b. p. 100—104°, containing small amounts of an unsaturated substance, is prepared by the action of magnesium ethyl iodide on sabinaketone; dilute sulphuric acid converts it into a *homologue* of terpineneterpin, which crystallises in white leaflets, m. p. 141—142°, and yields a *dihydrobromide*, $C_{11}H_{18},2HBr$, m. p. 88—89°, formed also by the action of hydrogen bromide on ethylsabinaketol in glacial acetic acid solution. The *dihydrochloride*, $C_{11}H_{18},2HCl$, crystallises in plates, m. p. 67—68°; the *dihydrobromide*, m. p. 88—89°; the *dihydriodide* forms prisms, m. p. 89—90°.

The action of zinc and ethyl bromoacetate on sabinaketone, elimination of water from the resulting *hydroxy*-ester, and subsequent hydrolysis of the unsaturated *ester* leads to the formation of the unsaturated *acid* (I), m. p. 47—48°. The *silver* salt, $C_{11}H_{15}O_2Ag$, was analysed. On distillation, the acid loses carbon dioxide, forming a *β-terpinene* (II), b. p. 176°, D 0·843, n_D 0·4773, which with hydrogen chloride in glacial acetic acid solution yields terpinene dihydrochloride, m. p. 52°, and is converted by nitrous acid into terpinene nitrosite.



(I.)



(II.)

G. Y.

Terpenes and Ethereal Oils. LXXXIX. OTTO WALLACH (*Annalen*, 1907, **357**, 72—84).—I. *Oxygenated Derivatives of Sylvestrene.*—The method previously described (this vol., i, 64) for substituting hydroxyl groups for halogen atoms in terpene compounds has now been applied to the formation of oxygenated derivatives of sylvestrene.

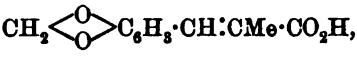
The prolonged action of hot aqueous potassium hydroxide on sylvestrene dihydrochloride leads to the formation of sylveterpineol, which distils with steam, in a 70% yield, and sylveterpin, which remains in the alkaline distillation residue in a 25% yield.

Sylveterpin, $C_{10}H_{18}(OH)_2$, separates from ethyl acetate in crystals, m. p. 135—136°, $[\alpha]_D$ +27·43°.

Sylveterpineol, $C_{10}H_{17}\cdot OH$, b. p. 210—214°, has an intense odour; with concentrated hydrochloric acid, it yields sylvestrene dihydrochloride, and is oxidised by 1% permanganate solution in the cold, yielding the *glycerol*, $C_{10}H_{17}(OH)_3$, which is obtained as a viscid, colourless oil, b. p. 165°/11 mm. This, on oxidation with chromic and dilute sulphuric acid, yields an *oil* which has an aldehyde-like odour, and reduces silver solutions.

Sylvecarvone, $C_{10}H_{14}O$, formed by removal of hydrogen chloride from sylvestrene nitrosochloride and hydrolysis of the resulting *oxime* by boiling oxalic acid, is obtained as an oil, and forms a *semicarbazone*, $C_{10}H_{14}:N\cdot NH\cdot CO\cdot NH_2$, crystallising in needles, m. p. 175—177°.

II. *Synthesis of Anethole from Anisaldehyde and of* iso*Safrole from Piperonal.*—[With EDGAR EVANS.]—The action of zinc and ethyl α-bromopropionate on anisaldehyde in benzene solution leads to the formation of the *hydroxy*-ester, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CHMe\cdot CO_2Et$, b. p. 235—245°/13 mm., which, when heated with potassium hydrogen sulphate at 150°, loses water and forms *ethyl β-anisyl-α-methylacrylate*, $OMe\cdot C_6H_4\cdot CH:CMe\cdot CO_2Et$, b. p. 170—180°/25 mm. The acid (Perkin, this Journ., 1877, i, 411), when slowly distilled, loses carbon dioxide and forms anethole.



β-Piperonyl-α-methylacrylic acid, $CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH:CMe\cdot CO_2H$, prepared in the same manner from piperonal and ethyl α-bromopropionate, when heated loses carbon dioxide and yields *iso*safrole.

III. *Occurrence of Sabinene in Ceylon Cardamom Oil and in Majorana Oil.*—A hydrocarbon, b. p. 165—167°, D 0·846, obtained from cardamom and majorana oils was considered previously (this vol., i, 64) to be sabinene. As this is now confirmed by oxidation of the hydrocarbon by means of permanganate with formation of sabinic acid, it is probable that the terpinene obtained from these oils by Weber (Abstr., 1887, 596) and Biltz (Abstr., 1899, i, 535) was formed by transformation of the sabinene present (this vol., i, 229).

IV. *Isomeric Camphenes and a New Camphenecamphoric Acid.*—[With PAUL GUTMANN.]—Various observations have suggested that naturally occurring camphene melts at a lower temperature than does synthetical camphene. To determine whether this difference results from the presence of impurities in the naturally occurring hydrocarbon or from the existence of different camphenes, the authors have investigated a camphene, m. p. 39°, b. p. 160—161°, D^{40} 0·8555,

$[\alpha]_D$ −84·9°, n_D^{40} 1·46207, obtained from Siberian pinewood oil. This, on oxidation with permanganate, yields a new *camphenecamphoric acid*, $C_{10}H_{16}O_4$, which crystallises in needles or leaflets, m. p. 142°, $[\alpha]_D$ −1·66°; the *silver* salt, $C_{10}H_{14}O_4Ag_2$, was analysed. On conversion into the *chloride* and treatment with ammonia, the acid yields the *amide*, $C_{10}H_{18}O_2N_2$, crystallising in needles, m. p. 197°. The *dianilide*, $C_{22}H_{26}O_2N_2$, m. p. 218°. The action of acetyl chloride on the acid in chloroform solution leads to the formation of a syrupy *anhydride*, which reacts with aniline, forming an *anilic acid*.

Small amounts of a *glycol* and of an *acid*, which forms a sparingly soluble *sodium* salt, are formed together with the camphenecamphoric acid by oxidation of the naturally occurring camphene. This is converted into *iso*borneol by Bertram's reaction, and forms a solid *hydrochloride*, which, on treatment with aniline, yields a camphene, m. p. 51°; on bromination by Reychler's method, the camphene, m. p. 39°, yields a *dibromide*, m. p. 89°. In view of these facts, the naturally occurring camphene is considered to be a physical isomeride of the synthetical hydrocarbon.

A specimen of camphene obtained from citronella oil yielded on oxidation the camphenecamphoric acid, m. p. 142°. Another camphene, m. p. 50°, b. p. 160—161°, $[\alpha]_D$ +103·89°, prepared by the action of sodium nitrite on pure bornylamine in acetic acid solution, on oxidation yields a camphenecamphoric acid, m. p. 141—142°, which is not identical with the acid obtained from the naturally occurring camphene.

G. Y.

Constituents of Ethereal Oils. Teresantalic Acid, $C_{10}H_{14}O_2$; a New Norcamphor and its Derivatives.

FRIEDRICH W. SEMMLER and KONRAD BARTELT (*Ber.*, 1907, 40, 4465—4472. Compare this vol., i, 703).—It has been shown by Müller (Abstr., 1900, i, 677) that teresantalic acid (I) is decomposed by sulphuric acid with formation of α-santene. An endeavour has now been made to study the course of this complicated reaction by employing formic in place of sulphuric acid. Here also the reaction is complicated, and leads to the formation of two products.

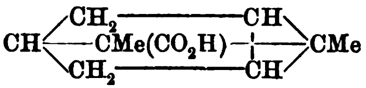
(*a*) The *formate* of π-norborneol, $C_{10}H_{16}O_2$, b. p. 87—94°/9 mm., D^{20} 1·0092, n_D 1·46559, $[\alpha]_D$ −10·15°, when boiled with alcoholic potassium hydroxide is hydrolysed to *π-norborneol* (II), m. p. 68—70°, b. p. 87—88°, which is optically inactive. The *acetate*, $C_{11}H_{18}O_2$, b. p. 89—90·5°/9 mm., D^{20} 0·987, n_D 1·45962.

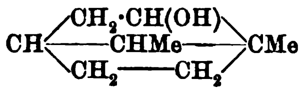
π-Norcamphor, $C_9H_{14}O$, formed by oxidation of π-norborneol with chromic acid in glacial acetic acid solution, has m. p. about 30°, b. p. 75—76°/9 mm., D^{20} 0·966, n_D 1·46900, is optically inactive, and on treatment with sodium and *iso*amyl formate in ethereal solution yields an *oxymethylene* derivative, $C_{10}H_{14}O_2$, b. p. 110—113°/9 mm., D^{20} 1·066, n_D 1·50045, which gives an intense bluish-violet coloration with ferric chloride.

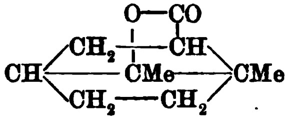
*π-Nor*iso*borneol*, $C_9H_{16}O$, m. p. 91—92°, b. p. 88°/9 mm., is prepared by reduction of the ketone with sodium and alcohol.

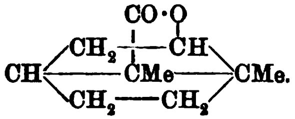
(*b*) The *lactone* (III), m. p. 190°, on reduction with sodium and alcohol forms a *glycol*, m. p. 254°, which when distilled with steam in presence of sulphuric acid yields a volatile *oxide*, $C_{10}H_{16}O$, m. p. 148°. The *hydroxy-acid*, $C_{10}H_{16}O_3$, m. p. 196°, corresponding to the lactone, forms a *methyl* ester, $C_{11}H_{18}O_3$, b. p. 125°/9 mm., D^{20} 1·098 n_D 1·48616.

The lactone (IV), m. p. 103°, obtained by Müller (*loc. cit.*) from teresantalic acid hydrochloride, is reduced to a *glycol*, $C_{10}H_{18}O_2$, b. p. 160—163°/10 mm. Hydrolysis of the lactone leads to the formation of a *hydroxy-acid*, $C_{10}H_{16}O_3$, m. p. 159°, which forms an ethyl ester, b. p. 120—123°/9 mm., D^{20} 1·089, n_D 1·48228.


(I.)


(II.)


(III.)


(IV.)

It remains undecided whether the two lactones and their hydroxy-acids are structurally or stereo-chemically isomeric. The constitutional formulæ given are ascribed to teresantalic acid and its derivatives on the former supposition, which necessitates the assumption that various hypothetical intermediate products are formed by the action of formic acid on teresantalic acid. G. Y.

The Present Position of the Chemistry of Rubber. SAMUEL S. PICKLES (*Brit. Assoc. Reports*, 1906, **76**, 233—257).—A résumé of the different methods employed in attacking the problem of the chemical constitution of rubber. G. T. M.

The Cyanogenetic Glucoside of Flax. (Linseed.) WYNDHAM R. DUNSTAN and THOMAS A. HENRY (*Bull. Acad. roy. Belg.*, 1907, 790—793). **Linamarin.** ARMAND JORISSEN (*ibid.*, 793—798).—Polemical, in reference to the question whether the name phaseolunatin or linamarin should be used for this glucoside (see Jorissen and Hairs, Abstr., 1885, 181; 1892, 502; Jouck, *Diss. Strasbourg*, 1902; Dunstan and Henry, Abstr., 1904 ii, 711; Jorissen, this vol., i, 434).
T. A. H.

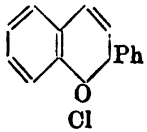
Bromo-derivatives of Dimethyl- and Trimethyl-furandicarboxylic Acids. HYPOLYT TREPHILIEFF (*Ber.*, 1907, **40**, 4388—4389).—Complicated changes occur when these acids are brominated in aqueous solution. Tetrabromo-derivatives are, however, obtained from methronic acid, ethyl methronate, and methyl methronate by exposing these substances to the action of bromine vapour at the ordinary temperature for two to three weeks. Nitric acid oxidises tetrabromomethronic acid to oxalic acid; lead peroxide oxidises this acid to succinic acid.

Condensation of maleic acid and ethyl acetoacetate in the presence

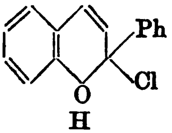
of acetic anhydride results in the formation of a *compound*, $C_{11}H_{14}O_5$, of m. p. 137°.
W. R.

Benzopyronium and Higher Homologous and Isologous Pyronium Rings.

HERMAN DECKER and THEODOR VON FELLENBERG (*Annalen*, 1907, 356, 281—342. Compare this vol., i, 950).—The oxygen-free salts of triphenylcarbinol having been recognised as carbonium salts, the constitution of the substances described as salts of xanthonium (Bünzly and Decker, Abstr., 1904, i, 912) and coeroxonium (Decker, Abstr., 1906, i, 687) and their sulphur isologues, and of dinaphthoxonium and coerdioxonium (Decker, *ibid.*, 874), became doubtful, since these possess the atomic groupings of di- and tri-phenylcarbinol and may equally be carbonium salts. In favour of the oxonium constitution is the difference in the basicities of triphenylcarbinol and phenylxanthanol; whilst salts of the former are not formed by the action of hydrochloric acid and are decomposed by 70% sulphuric acid, phenylxanthonium salts are stable in 10% sulphuric acid and are readily formed by means of hydrochloric acid. Moreover, the sulphur isologues are more strongly basic than the oxygen compounds in agreement with the known greater stability of thionium than oxonium salts. It is now found that the action of magnesium phenyl bromide on coumarin or of concentrated hydrochloric acid on *o*-hydroxybenzylideneacetophenone leads to the formation of a substance which must be 2-phenylpyronium chloride (I), as a substance having the other possible constitution (II) would not be a salt:



(I.)



(II.)

It is argued that as the benzopyronium salts are isologues of the quinolonium series, so the salts of xanthonium and thioxanthoniume must be isologous with the acridonium and those of coeroxonium and coerthionium with the coeramidonium (Decker, Ferrario, and Schenk, Abstr., 1906, i, 690) derivatives. The preparation and properties of a number of salts of benzopyronium, xanthonium, coeroxonium, and their isologues are described.

Benzopyronium chloride, prepared by heating gluco-*o*-coumaraldehyde with concentrated hydrochloric acid, is readily soluble; the *ferrichloride*, $C_9H_7OCl,FeCl_3$, forms a yellow, crystalline powder, m. p. 199° (corr.), and when heated with aqueous acetone gives an odour of fennel; the *aurichloride*, $C_9H_7OCl,AuCl_3$, crystallises in brownish-yellow, microscopic needles, m. p. 198—200° (corr.).

2-*Methylbenzopyronium ferrichloride*, $C_{10}H_9OCl,FeCl_3$, prepared from *o*-hydroxycinnamyl methyl ketone, crystallises in yellow needles, m. p. 118—119° (corr.). The *cadmiobromide*, $C_{10}H_8OBr,CdBr_2$, forms a yellow, crystalline powder. The free *base* is unstable and readily changes into a *dye*. The *iodide*, $C_{10}H_9OI$, prepared from coumarin and magnesium methyl iodide, crystallises in greenish-brown needles,

m. p. 56—60°, readily loses iodine, and when heated with aqueous sulphurous acid is decomposed, forming coumarin.

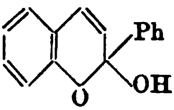
2-*Phenylbenzopyronium chloride*, $C_{15}H_{11}OCl$, crystallises in yellow leaflets, m. p. 69—70° (corr.), and is hygroscopic. The *ferrichloride*,

$$C_{15}H_{11}OCl,FeCl_3,$$

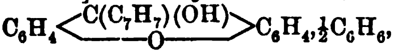
yellow needles, m. p. 125—129° (corr.), *aurichloride*,

$$C_{15}H_{11}OCl,AuCl_3,$$

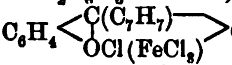
m. p. 200—202°, *mercurichloride*, brownish-yellow needles, m. p. 183—185°, *cadmiobromide*, $C_{15}H_{11}OBr,CdBr_2$, brownish-yellow needles, m. p. 190—192°, *perbromide*, $C_{15}H_{11}OBr,Br_2$, orange-red crystals, m. p. 122°, *periodide*, $C_{15}H_{11}OI,I_2$, m. p. 147—148°, unstable, and *iodide*, orange-red crystals, are described. A *by-product* from the action of magnesium phenyl bromide on coumarin, which is insoluble in hydrochloric acid, will be described later (compare Houben, Abstr., 1904, i, 302, 334). The action of sodium hydroxide and much water on the chloride leads to the formation of a greenish-brown precipitate containing the *carbinol base*, which has the annexed constitution, and is obtained also by the action of ammonia on the chloride in ethereal solution.

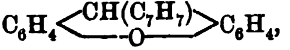


[With FRITZ DINNER.]—9-o-*Tolylxanthen*-9-*ol*,



$$C_6H_4{<}\begin{matrix}C(C_7H_7)(OH)\\O\end{matrix}{>}C_6H_4,\tfrac{1}{2}C_6H_6,$$

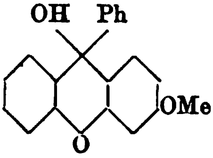
prepared from xanthone and magnesium *o*-tolyl bromide (compare Bünzly and Decker, *loc. cit.*), crystallises from benzene in colourless needles, and loses $\frac{1}{2}C_6H_6$ at 110°; m. p. 150·5°. o-*Tolylxanthonium ferrichloride*,  $C_6H_4{<}\begin{matrix}C(C_7H_7)\\OCl(FeCl_3)\end{matrix}{>}C_6H_4$, crystallises in yellowish-brown needles, m. p. 208—209°. o-*Tolylxanthen*,



$$C_6H_4{<}\begin{matrix}CH(C_7H_7)\\O\end{matrix}{>}C_6H_4,$$

prepared by boiling *o*-tolylxanthenol with hydriodic acid and red phosphorus in acetic anhydride solution, crystallises in colourless needles, m. p. 119°, and dissolves in cold sulphuric acid, forming the xanthonium salt. A *substance*, $C_{23}H_{19}O_2$ or $C_{23}H_{20}O_2$, crystallises in large plates, m. p. 162°, a *hydrocarbon*, $(C_{14}H_{13})_x - (C_9H_8)_x$, m. p. 214°, and a *substance*, crystallising in leaflets, m. p. 170°, are obtained as by-products of the action of magnesium *o*-tolyl bromide on xanthone.

3-*Methoxy*-9-*phenylxanthonium ferrichloride*, $C_{20}H_{15}O_2Cl,FeCl_3$, prepared from 3-methoxyxanthone and magnesium phenyl bromide, forms dark red crystals, m. p. 124°, and on treatment with water yields 3-*methoxy*-9-*phenylxanthen*-9-*ol*, m. p. 133°. This has the annexed constitution, and with acids yields oxonium salts which are stable in 10% hydrochloric acid and form deep red, fluorescent solutions.



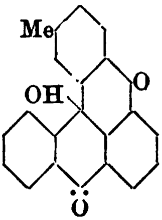
2-*Methoxy*-9-*phenylxanthonium ferrichloride*, prepared from 2-methoxyxanthone, crystallises in needles, m. p. 154°, and is more stable to water and more deeply coloured than its isomeride.

[With Enos Ferrario.]—The green, fluorescent solution obtained on dissolving fluoran in concentrated sulphuric acid contains 9-o-*carboxyphenylxanthonium sulphate*, which is stable only in the concentrated acid. The *ferrichloride*, $CO_2H\cdot C_6H_4\cdot C_{13}H_8OCl,FeCl_3$, prepared by adding hydrochloric acid containing solid ferric chloride to a hot solution of fluoran in acetic acid, crystallises in yellow needles, m. p. 200°. Fluoran does not form a xanthonium salt with fuming hydrochloric acid; this difference in behaviour from the other members of the group results, not only from the negative influence of the carboxylic group, but also from the tendency of the carbinol base to lactone formation.

Dimethylfluoran forms a *xanthoniumferrichloride*, $C_{22}H_{17}O_3Cl,FeCl_3$, crystallising in orange needles, m. p. 215°.

Coeroxonol (Abstr., 1906, i, 688) forms ethers when boiled with the corresponding alcohols. The *methyl ether*, $C_{21}H_{14}O_3$, crystallises in colourless needles, m. p. 133°. The n-*propyl ether*, $C_{23}H_{18}O_3$, m. p. 151°. The iso*butyl ether*, $C_{24}H_{20}O_3$, m. p. 132°. These ethers are convertible into each other; thus the methyl ether is formed when the ethyl ether is boiled with a large excess of methyl alcohol. Coeroxonol condenses readily with acetone, forming *acetonylcoeroxone*, m. p. 146°, which yields coeroxonium salts when heated with hydrochloric or sulphuric acid.

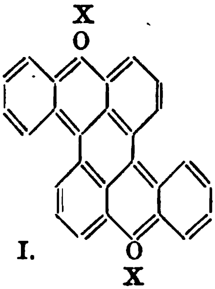
[With Leo Stern.]—*Erythroxyanthraquinone* p-*tolyl ether*, $C_{21}H_{14}O_3$, prepared as described in D.R.-P. 158531 (Abstr., 1905, i, 797), crystallises in yellow needles, m. p. 128·5°, and, when heated with fuming sulphuric acid and treated with ferric chloride, yields 14-*methylcoeroxonium ferrichloride*, $C_{21}H_{13}O_2Cl,FeCl_3$, which is obtained in reddish-brown crystals, m. p. 232·5—235·5°, has the properties characteristic of coeroxonium salts, and becomes colourless on treatment with water. 14-*Methylcoeroxone*-9-*ol* (annexed formula) separates from benzene in colourless crystals, m. p. 176°, and reacts with acids, forming the dark red oxonium salts. The *ethyl ether*, $C_{23}H_{18}O_3$, crystallises in needles, m. p. 139°.



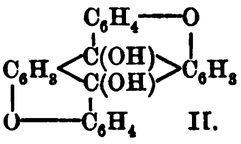
[With Enos Ferrario.]— 4 : 14-Dimethylcoeroxone-9-ol, previously described (Abstr., 1906, i, 688) as 3 : 13-dimethylcoeroxonol, has m. p. 170° (152° : *loc. cit.*). The *methyl ether*, $C_{23}H_{18}O_3$, forms colourless crystals, m. p. 105°. The *ethyl ether*, $C_{24}H_{20}O_3$, m. p. 145°. The action of mineral acids on the carbinol leads to the formation of oxonium salts; the ferrichloride, m. p. 210° (160° : *loc. cit.*). Reduction of the carbinol base or of the oxonium salts leads to the formation of 4 : 14-*dimethylcoeroxen*-10-*ol*, which has a strong green fluorescence, dissolves in aqueous sodium hydroxide, forming an orange-red solution, and is very readily oxidised. The *acetate* is obtained in yellow crystals, m. p. 230°.

[With August Würsch.]—1-*Thiolanthraquinone* p-*tolyl ether*, $C_{21}H_{14}O_2S$, prepared from potassium α-anthraquinonesulphonate, *p*-thiocresol, and potassium hydroxide, or from nitroanthraquinone, crystallises in orange-red needles, 223—225°, and when heated with fuming sulphuric acid yields the 14-*methylcoerthionium* salt, which is isolated as the *ferrichloride*, $C_{21}H_{13}OSCl,FeCl_3$, obtained in blackish-green crystals, m. p. 240°. 14-*Methylcoerthione*-9-*ol*, $C_{21}H_{14}O_2S$, formed by the action of water on the thionium salt, separates from benzene as a white, crystalline powder, m. p. 235°, and on reduction yields 14-*methylthiene*-10-*ol*, $C_{21}H_{14}OS$, m. p. 247°, which forms yellow solutions with green fluorescence, and is soluble in alkalis.

[With ENOS FERRARIO.]—When heated with phosphoric acid or a mixture of phosphoric and sulphuric acids, anthrarufin diphenyl ether is converted into coerdioxonium salts having the constitution (I). The *ferrichloride*, $C_{26}H_{14}O_2Cl_2,2FeCl_3$, is obtained as a black, crystalline precipitate. The *sulphate*, *hexabromide*, and *iodide* are described. When treated with water, the ferrichloride yields *coerdioxendiol* (II), which separates as a violet, crystalline powder, forms violet-blue to violet-red solutions with intense, brownish-red fluorescence, and is reduced to *coerdioxen*. This forms an orange-red precipitate, sublimes, forming a red sublimate, dissolves in ether or benzene to an orange solution with intense green fluorescence, and is readily oxidised, yielding the dioxonium salts.



I.



$$\begin{array}{l} \qquad C_6H_4\text{——}O \\ \qquad\ \ | \qquad\qquad | \\ C_6H_3{<}\begin{matrix}C(OH)\\C(OH)\end{matrix}{>}C_6H_3 \\ | \qquad\quad\ \ | \\ O\text{——}C_6H_4 \end{array}$$

II.

1 : 5-*Dithiolanthraquinone diphenyl ether*, $C_{26}H_{16}O_2S_2$, prepared by boiling dinitroanthraquinone, thiophenol, and potassium hydroxide in alcoholic solution, crystallises in orange-red plates, m. p. 247°, and on prolonged heating at 200° and treatment with sulphuric acid and ferric chloride yields *coerdithionium ferrichloride*, $C_{26}H_{14}S_2Cl_2,2FeCl_3$, which forms black crystals, with a green shade when powdered, m. p. 258—260°; the *hexabromide* forms an olive-green precipitate. *Coerdithiendiol*, formed by the addition of water to the coerdithionium salts, separates from glacial acetic acid in colourless crystals, m. p. 248°, yields a coloured, fluorescent solution if strongly heated in acetic acid, and is reduced to *coerdithien*, which is obtained as an orange precipitate, sublimes unchanged, forms fluorescent solutions, and is readily oxidised to the dithionium salts.

1 : 5-*Dithiolanthraquinone di*-p-*tolyl ether*, $C_{28}H_{20}O_2S_2$, prepared from thio-*p*-cresol, potassium hydroxide, and dinitroanthraquinone, forms reddish-brown crystals, m. p. 249°. *Dimethylcoerdithionium ferrichloride* forms black crystals, m. p. 204°. *Dimethylcoerdithenol* is colourless. *Dimethylcoerdithien* is yellowish-red, forms solutions with green fluorescence, and is readily oxidised to the dithionium salts.

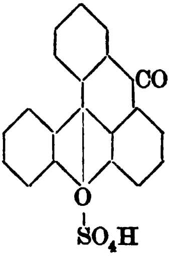
The isologous coerdiamidonium compounds have been previously described (Farbenfabriken vorm. Friedr. Bayer & Co., Abstr., 1902, i, 501).

The relation of the coeroxonium salts to the coeroxonols and the similar relations in the isologous series are discussed in the light of Thiele's theory of partial valencies. G. Y.

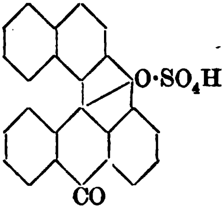
Preparation of Coeroxonium and Coerthionium Derivatives.

FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 186882. Compare Abstr., 1905, i, 797; 1906, i, 687).—The aryl ethers and aryl thioethers of the anthraquinone series when condensed with neutral or acid dehydrating agents give rise to coeroxonium and coerthionium derivatives, which are used in the preparation of colouring matters.

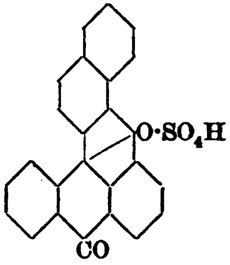
Coeroxonium sulphate (I) results from the dehydrating action of 70% sulphuric acid or zinc chloride on 1-phenoxyanthraquinone (erythroxyanthraquinone phenyl ether):



(I.)



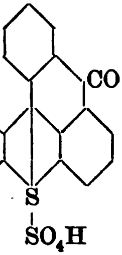
(II.)



(III.)

The free coeroxonium base (coeroxonol; *loc. cit.*), a white, crystalline precipitate, is set free from the sulphate by ammonia; its ethyl ether, $C_{22}H_{16}O_3$, m. p. 145°, is a well-defined, crystalline substance.

Coeroxonium ferrichloride, $C_{20}H_{11}O_2Cl,FeCl_3$, m. p. 233°, is obtained in dark red crystals on adding ferric chloride and strong hydrochloric acid to the sulphate solution.



(IV.)

Benzocoeroxonium salts are obtained when the β-naphthyl ether of 1-hydroxyanthraquinone are employed in the foregoing condensation.

Benzocoeroxonium sulphate (II), the corresponding *chloride*, and the *ferrichloride*, $C_{24}H_{13}O_2Cl,FeCl_3$, are sparingly soluble, dark violet, crystalline salts. The free base, *benzocoeroxonol*, m. p. 186—187°, separates in almost colourless crystals.

iso*Benzocoeroxonium sulphate* (III) is obtained in a similar manner from α-naphthyl-1-oxyanthraquinone.

Coerthionium sulphate (IV) is a violet-red salt resulting from the condensation of phenyl-1-thioanthraquinone; its carbinol base may be crystallised from alcohol. The coerthionium salts are generally more intensely coloured than the corresponding coeroxonium derivatives. G. T. M.

Action of Grignard's Reagent on Cinchonicine. EZIO COMANDUCCI (*Boll. chim. Farm.*, 1907, 46, 753—756).—With magnesium ethyl iodide, cinchonicine yields a pale yellow, amorphous, additive *compound*, which is stable when kept in a sealed tube or over sulphuric acid. This compound no longer contains the ketonic or vinyl group, and, when treated with dilute sulphuric acid, it yields a product which, after repeatedly dissolving in hydrochloric acid and precipitating with ammonia, has the composition $NH:C_{16}H_{18}N(CEt·OH)·CH_2·CH_2Et$ or $NH:C_{16}H_{18}N(CEt·OH)·CHMeEt$. T. H. P.

Action of Halogen on Morphine Derivatives. EDUARD VONGERICHTEN and O. DENSDORFF (*Ber.*, 1907, 40, 4146—4154).—A continuation of the work of Vongerichten and Hübner (this vol., i, 718), who studied the action of bromine on morphine, codeine, α- and β-methylmorphimethines and dihydromethylmorphimethine respectively.

Acetyl-α-methylmorphimethine, in dilute acetic acid solution, behaves like α-methylmorphimethine in uniting with only 1 mol. of bromine; in more concentrated acetic acid solution, 3 atoms of bromine are added on. *Acetyldibromodihydro-α-methylmorphimethine hydrobromide*, $C_{21}H_{25}O_4NBr_2,HBr$, has m. p. about 202° (decomp.); the *platinichloride*, $(C_{21}H_{24}O_4NBr)_2,H_2PtCl_6$, was prepared. By the action of sodium methoxide on acetylbromo-α-methylmorphimethine, *bromo-α-methylmorphimethine* was obtained; the *platinichloride*,

$$(C_{19}H_{22}O_3NBr)_2,H_2PtCl_6,$$

and the *methiodide* $C_{19}H_{22}O_3NBr,MeI$, were prepared.

Acetylbromoiso-α-methylmorphimethine hydrobromide,

$$C_{21}H_{24}O_4NBr,HBr,$$

obtained by boiling acetyldibromodihydro-α-methylmorphimethine hydrobromide with acetic anhydride, separates from water in glistening needles, decomposing at 235°.

Acetylnor-p-*thebaine methobromide*, $C_{21}H_{24}O_4NBr$, obtained by heating acetoxybromodihydro-α-methylmorphimethine with acetic anhydride, crystallises in needles or prisms, m. p. 231—233°. *Acetylnor*-p-*thebaine methiodide*, formed by the addition of potassium iodide to the preceding compound, has m. p. 236°. *Nor*-p-*thebaine methiodide*, $C_{19}H_{22}O_3NI$, has m. p. 220°. A. McK.

Preparation of Sulphonic Acids of Acetyl Derivatives of Morphine. KNOLL & Co. (D.R.-P. 195601. Compare this vol., i, 235).—When morphine is gently heated with a mixture of acetic anhydride and sulphuric acid which no longer gives the reactions of sulphuric acid, it is converted into triacetylmorphine. When, however, the reaction is carried out at temperatures lower than that required to convert acetyl sulphuric acid into sulphoacetic acid, then the base is simultaneously acetylated and sulphonated. The product, *diacetylmorphinesulphonic acid*, is precipitated by ether from its aqueous or alcoholic solutions as a white powder, which on acidifying separates from its alkaline solution in clusters of needles not melting below 280°. As is generally the case, the introduction of the sulphonic group greatly diminishes the toxic action of morphine. G. T. M.

Intermediate Product in the Formation of *apo*Morphine. LORENZ ACH and HERMANN STEINBOCK (*Ber.*, 1907, **40**, 4281—4285).—The restricted action of hydrochloric acid on morphine yields a compound, termed by the authors β-chloromorphide, which is isomeric with Schryver and Lees' chloromorphide (Trans., 1900, **77**, 1024), and can also be prepared from the latter by the gentle action of hydrochloric acid.

β-Chloromorphide, $C_{17}H_{18}O_2NCl$, crystallises from ether in a drusy mass of prisms or from alcohol in prisms, m. p. 188°, and is more readily soluble in alcohol or benzene than its isomeride. When freshly precipitated from its salts, β-chloromorphide is readily soluble in ether, but after one crystallisation it dissolves only sparingly in this solvent.

Its salts are mostly readily soluble, but the *nitrate* separates easily in prisms. With sulphuric acid, it yields a *sulpho*-derivative,

$$C_{17}H_{18}O_5NClS,$$

which crystallises from water in glassy prisms containing $1H_2O$, and has a neutral reaction in aqueous solution; the sulpho-compound yields a crystalline *acetyl* derivative, and, when heated with water at 140°, it is converted into a crystalline *sulpho*-compound free from chlorine.

The isomeric chloromorphide (*loc. cit.*) yields no crystalline sulpho-derivative.

β-Chloromorphide methiodide, $C_{18}H_{21}O_2NClI$, separates from water in dense crystals, m. p. 210° (decomp.), and is decomposed when heated with an aqueous alkali, yielding a volatile base.

Acetyl-β-chloromorphide, $C_{19}H_{20}O_3NCl$, crystallises from alcohol in needles, m. p. 163°, and yields a *methiodide*, m. p. 177° (decomp.).

T. H. P.

Preparation of Additive Products of Alkylnarceine or Alkylhomonarceine and their Alkyl Ethers. KNOLL & Co. (D.R.-P. 186884. Compare this vol., i, 236).—*Methylnarceine methosulphate*,

$$C_{23}H_{26}MeO_8NMe\cdot SO_4Me,$$

m. p. 184—186°, formed by the interaction of narceine (1 mol.) and methyl sulphate (2 mols.) in alcoholic potassium hydroxide; its hydrochloride decomposes at 196°. The following compounds are also described. *Ethylnarceine ethiodide*, $C_{23}H_{26}EtO_8NEtI$, m. p. 140—144°, produced by the combination of ethylnarceine and ethyl iodide at 80°; *diethylnarceine methiodide*, $C_{23}H_{25}Et_2O_8NMeI$, m. p. 184—185°; *dimethyl methylnarceine methophosphate*, $C_{23}H_{26}MeO_8NMe\cdot PO_4Me_2$, its hydrochloride, m. p. 136°; *methylnarceine methobenzenesulphonate*,

$$C_{23}H_{26}MeO_8NMe\cdot SO_3Ph,$$

hydrochloride, m. p. 136°; *methylnarceine methonitrate*,

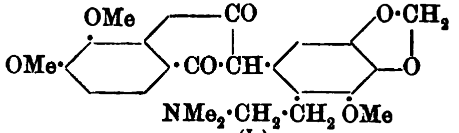
$$C_{23}H_{26}MeO_8NMe\cdot NO_3.$$

G. T. M.

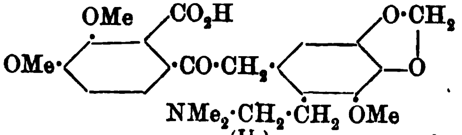
Preparation of *apo*Narceine. KNOLL & Co. (D.R.-P. 187138. Compare this vol., i, 236).—*apo*Narceine (I), yellow needles, m. p. 112—115°, is obtained by treating narceine (II) with dehydrating agents, such as mineral acids, acid chlorides, or acid anhydrides; it is extracted with ether and converted into its *hydrochloride*,

$$C_{23}H_{25}O_7N,HCl,H_2O,$$

yellow needles, m. p. 144°. This salt is only sparingly soluble in cold water, but dissolves more readily on warming; it gives the ordinary alkaloid reactions. *apo*Narceine is insoluble in water, but dissolves readily in the ordinary



(I.)



(II.)

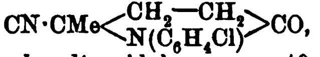
organic media, excepting light petroleum; when warmed with alkalis, it is reconverted into narceine. The *apo*narceine *methosulphate* crystallises from alcohol and ether in needles; it forms similar additive compounds with other alkyl halides, sulphates, and phosphates.

G. T. M.

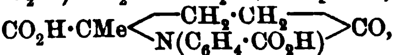
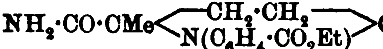
Anisotheobromine. VON SZTANKAY (*Chem. Zentr.*, 1907, i, 1806; from *Pharm. Post*, 1907, **40**, 322).—*Anisotheobromine* (*sodium theobromine anisate*), $NaC_7H_7O_2N_4,OMe\cdot C_6H_4\cdot CO_2Na$, is a white, slightly deliquescent powder, melting and decomposing when carefully heated. Acids precipitate theobromine and anisic acid from its aqueous solution.

W. H. G.

Condensation Products of Ethyl Lævulate, Hydrogen Cyanide, and Para-substituted Anilines. HERMANN WEBER (*Ber.*, 1907, **40**, 4044—4052. Compare Kühling and Falk, Abstr., 1905, i, 372).—The author's aim is to ascertain the influence of negative substituents on the stability of the pyrrolidone nucleus. The condensations are carried out in alcoholic solution on the water-bath. 1-p-*Chlorophenyl-2-methylpyrrolidone-2-carboxylonitrile*,



$$CN\cdot CMe{<}\begin{matrix}CH_2-CH_2\\ N(C_6H_4Cl)\end{matrix}{>}CO,$$

the *amide*, and the *carboxylic* acid have m. p. 40—42°, 207°, and 179° respectively. The corresponding *compounds*, obtained from *p*-bromoaniline, have m. p. 49—51°, 208°, and 189° respectively; the *barium* and *silver* salts and the *methyl* ester were prepared. The nitrile yields a thioamide with ammonium sulphide, and γ-oximinovaleric acid by treatment with hydroxylamine hydrochloride. 1-p-*Iodophenyl-2-methylpyrrolidone-2-carboxylonitrile* is an oil, from which the *amide*, m. p. 222°, and the *carboxylic* acid, m. p. 211—212°, are readily obtained. *p*-Aminobenzonitrile condenses with hydrogen cyanide and ethyl lævulate to form an oil from which well-defined derivatives have not been obtained. Ethyl *p*-aminobenzoate condenses readily to form the *substance*, $CN\cdot CMe(NH\cdot C_6H_4\cdot CO_2Et)\cdot CH_2\cdot CH\cdot CO_2Et$, m. p. 75°, from which the *dicarboxylic acid*,  $CO_2H\cdot CMe{<}\begin{matrix}CH_2\cdot CH_2\\ N(C_6H_4\cdot CO_2H)\end{matrix}{>}CO$, m. p. 228—229°, is obtained by hydrolysis; the *ethyl ester-amide*,  $NH_2\cdot CO\cdot CMe{<}\begin{matrix}CH_2\cdot CH_2\\ N(C_6H_4\cdot CO_2Et)\end{matrix}{>}CO$, has m. p. 149°, and the corresponding *methyl ester-amide*, 171—172°.

C. S.

[Preparation of Amino-Ethers.] EMANUEL MERCK (D.R.-P. 184968).—The amino-ethers having the general formula

$$Z{:}N\cdot[CH_2]_x\cdot O\cdot R$$

are obtained by treating the halogenated ethers, $X\cdot[CH_2]_x\cdot O\cdot R$, with secondary amines. The hydrochlorides of these amino-ethers give neutral solutions and have a powerful anæsthetic action.

Guaiacyl ϵ-dimethylaminoamyl ether, $OMe\cdot C_6H_4\cdot O\cdot[CH_2]_5\cdot NMe_2$, m. p. 144—145°, was produced by mixing guaiacyl ϵ-bromoamyl ether with dimethylamine in closed vessels; its hydrochloride is soluble. *γ-Piperidylpropyl phenyl ether*, $Ph\cdot O\cdot[CH_2]_3\cdot C_5NH_{10}$, b. p. 150°/10 mm., *ε-Piperidylamyl phenyl ether*, $Ph\cdot O\cdot[CH_2]_5\cdot NC_5H_{10}$, b. p. 172°/3 mm. *γ-Piperidylpropyl guaiacyl ether*, $OMe\cdot C_6H_4\cdot O\cdot[CH_2]_3\cdot NC_5H_{10}$, b. p. 173°/10 mm. *ε-Piperidylamyl guaiacyl ether*,

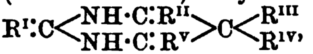
$$OMe\cdot C_6H_4\cdot O\cdot[CH_2]_5\cdot NC_5H_{10},$$

b. p. 190°/5 mm. *ε-Piperidylamyl menthyl ether*,

$$C_{10}H_{18}\cdot O\cdot[CH_2]_5\cdot NC_5H_{10},$$

b. p. 170—172°/4 mm. *ε-Piperidylpropyl thymyl ether*, b. p. 197°/6 mm. *ε-Piperidylamyl thymyl ether*, b. p. 200—202°/8 mm., and *ε-camphidinylamyl thymyl ether*, $C_{10}H_{13}\cdot O\cdot[CH_2]_5\cdot NC_{10}H_{18}$, hydrochloride, m. p. 122—123°, were all prepared in a similar manner from the corresponding brominated mixed ethers. G. T. M.

Preparation of Pyrimidine Derivatives. EMANUEL MERCK (D.R.-P. 185963).—Pyrimidine derivatives having the general formula:



$$R^{I}{:}C{<}{\begin{matrix}NH\cdot C{:}R^{II}\\NH\cdot C{:}R^{V}\end{matrix}}{>}C{<}{\begin{matrix}R^{III}\\R^{IV}\end{matrix}},$$

are obtained by condensing carbamide, thiocarbamide, guanidine, or their derivatives with alkyl malonates, malonamates, or cyanoacetates, or with malononitrile, or mono- and di-alkyl derivatives of substituted malonic acids in the presence of the carbides of the alkali or alkaline earth metals.

4-Iminobarbituric acid results from the condensation of carbamide, ethyl cyanoacetate, and sodium carbide in xylene solution, being precipitated from the resulting alkaline solutions with acetic acid. 5:5-Diethylbarbituric acid is similarly obtained from carbamide, ethyl diethylmalonate, and sodium carbide. G. T. M.

Hydroxylopyridinechromium Salts. Additive Salt Formation with Metallic Hydroxides. PAUL PFEIFFER [and W. OSANN] (*Ber.*, 1907, **40**, 4026—4036).—The monohydroxylo-, dihydroxylo-, and trihydroxylo-compounds, derived from chromiumtetra-aquodipyridine, were found to form salts with acids by direct addition (Abstr., 1906, i, 531). Such additive salt formation has been studied also in the case of other metallic hydroxides (this vol., i, 895; ii, 694; Werner, this vol., i, 189, 239; ii, 560). The present paper contains an account of further observations made with members of the pyridinechromium series.

The hydroxylo-salts, derived from chromiumtetra-aquodipyridine, are prepared by three methods: (1) the removal of a mol. of acid from an aquo-salt by the action of a base; (2) the gradual addition of an acid to a polyhydroxylo-compound, which leads finally to the formation of the tetra-aquo-salt, and (3) the action of normal salts on tetra-aquo-salts in aqueous solution, which leads only in certain cases to the formation of hydroxylo-salts in consequence of partial hydrolysis of the tetra-aquo-salt in solution.

Hydroxylotriaquodipyridinechromium thiocyanate and sulphate have now been prepared by the action of ammonium thiocyanate and sulphate respectively on dihydroxylodiaquodipyridinechromium chloride in acetic acid solution.

Dihydroxylodiaquodipyridinechromium iodide, $[CrPy_2(OH_2)_2(OH)_2]I$, formed by addition of potassium iodide to the dihydroxylo-chloride in acetic acid solution or to the monohydroxylothiocyanate in aqueous solution, or of hydriodic acid to chromiumtrihydroxyloaquodipyridine, is obtained as a greenish-grey powder, and on treatment with a mineral acid yields the corresponding tetra-aquo-salt.

Dihydroxylodiaquodipyridinechromium thiocyanate,

$$[CrPy_2(OH_2)_2(OH)_2]SCN,$$

prepared by adding pyridine to the monohydroxylo-thiocyanate in presence of water, or by addition of ammonium thiocyanate to an aqueous solution of a soluble dihydroxylo-salt, forms a greyish-brown powder, has a slight alkaline reaction in aqueous solution, and forms the red tetra-aquo-salt on treatment with mineral acids.

Dihydroxylodiaquodipyridinechromium sulphate forms a greyish-green aqueous solution, which appears reddish-brown in thick layers, becomes red on addition of mineral acids, and yields the chloride and iodide as greyish-green precipitates on addition of sodium chloride and potassium iodide respectively.

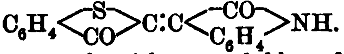
Dihydroxylodiaquodipyridinechromium nitrate,

$$[CrPy_2(OH_2)_2(OH)_2]NO_3,$$

is formed when chromiumtrihydroxyloaquodipyridine is treated with a small amount of nitric acid, or by the action of pyridine on tetra-aquodipyridinechromium nitrate in aqueous solution; it is obtained as a bluish-grey powder, has a very slight alkaline reaction, does not form silver oxide with aqueous silver nitrate, gives precipitates of the corresponding dihydroxylo-salts when treated with sodium chloride, potassium bromide and iodide, and ammonium thiocyanate, and is converted into red tetra-aquo-salts by the action of mineral acids.

Tetra-aquodipyridinechromium nitrate, $[CrPy_2(OH_2)_4](NO_3)_3$, prepared by addition of concentrated nitric acid to the preceding salt and evaporation over soda-line, forms light red leaflets, is deliquescent, dissolves, forming red solutions in water and alcohol, and gradually decomposes to a dirty green, viscid mass. G. Y.

[Preparation of Isatin Derivatives.] Kalle & Co. (D.R.-P. 182260 and 182261).—The condensation of isatin and 3-oxy-1-thionaphthen in hot aqueous sodium carbonate leads to the production of a very sparingly soluble colouring matter, having probably the constitution:



$$C_6H_4{<}\genfrac{}{}{0pt}{}{S}{CO}{>}C{:}C{<}\genfrac{}{}{0pt}{}{CO}{C_6H_4}{>}NH.$$

This substance furnishes a soluble reduction product on treatment with alkaline reducing agents. When isatinacetic acid is substituted for isatin in this condensation, a colouring matter is produced which furnishes a soluble sodium salt separating in lustrous, bright red crystals. This substance is a wool dye of considerable fastness.

G. T. M.

Asymmetric Nitrogen. XXX. Resolution of a Cyclic Asymmetric Ammonium Base. Edgar Wedekind and O. Wedekind (*Ber.*, 1907, 40, 4450—4456. Compare Buckney, this vol., i, 722).—The authors have resolved methylallyltetrahydroquinolinium *d*-bromocamphorsulphonate by recrystallisation from a mixture of solvents. The less soluble *l*-base *d*-acid salt has $[\alpha]_D + 39{\cdot}09^\circ$, $[M]_D + 194{\cdot}7^\circ$, and on treatment with concentrated aqueous potassium iodide yields the *iodide*, $[\alpha]_D + 20{\cdot}57^\circ$, $[M]_D - 64{\cdot}98^\circ$, which rapidly undergoes racemisation when dissolved in methyl alcohol. The more soluble *d*-base *d*-acid salt has $[\alpha]_D$ +76·48°, $[M]_D$ +380·7°. These values give $[M]_D$ −80·3° and +105·7° for the *l*- and *d*-basic ions respectively. On further fractional recrystallisation, a fraction having $[M]_D$ +434° was obtained; this yields an iodide which after recrystallisation is optically inactive.

Benzylmethyltetrahydroquinolinium bromide undergoes partial decomp. when recrystallised. The d-*bromocamphorsulphonate* crystallises in colourless prisms, m. p. 180° (decomp.). Attempts to resolve this salt were unsuccessful (compare Jones, Trans., 1903, **83**, 1417).

[With Robert Oechslen.]—*Ethyl* N-*methyltetrahydroquinolinium-acetate* d-*camphorsulphonate*, $C_{24}H_{35}O_6NS$, prepared from the *iodide*, crystallises in colourless needles, decomp. about 95°, $[\alpha]_D$ +11·7°, $[M]_D$ +51·9°, and is hygroscopic. Attempts to resolve this salt also were fruitless. G. Y.

Carbazole. Gustav Schultz and L. Hauenstein (*J. pr. Chem.*, 1907, [ii], **76**, 336—349).—An investigation of the sulphonic acids of carbazole (compare Graebe and Glaser, this Journ., 1872, **25**, 302; Bechhold, Abstr., 1890, 1297; Wirth and Schott, Abstr., 1903, i, 54). —Carbazole is sulphonated slowly at the ordinary temperature, more rapidly at 70—75°, by concentrated sulphuric acid; the reaction product contains di- and tri-sulphonic acids together with unchanged carbazole. The disulphonic acid is isolated as the *barium* salt, $C_{12}H_7N(SO_3)_2Ba,3H_2O$, which loses $2H_2O$ in a desiccator, and becomes anhydrous at 180—190°. The free *acid* is obtained as a transparent, compact mass, m. p. below 56°, becomes blue on the surface, gives a brown coloration when fused with resorcinol, and on fusion with oxalic acid forms a blue *dye* soluble in water. The *sodium*, $C_{12}H_7N(SO_3Na)_2$, and *potassium* salts were analysed. *Carbazole-disulphonyl chloride*, $C_{12}H_7N(SO_2Cl)_2$, prepared by heating the potassium salt with phosphorus pentachloride in a water-bath, is hydrolysed by hot water, and reacts with ammonia, forming the *disulphonamide*, $C_{12}H_7N(SO_2{\cdot}NH_2)_2$, which crystallises in colourless needles or triangular plates, m. p. 220—225°. The sulphonic acid groups of carbazoledisulphonic acid are displaced only with difficulty; the acid remains almost unchanged when heated with alkalis at 250°, but yields a *phenolic* product at 300—320°. Distillation of the potassium disulphonate with potassium ferrocyanide or cyanide leads to the formation of carbazole. When heated with concentrated nitric acid on the water-bath, the potassium disulphonate yields *potassium tetranitrocarbazolesulphonate*, which crystallises in yellow needles.

Potassium nitrocarbazoledisulphonate, $C_{12}H_6O_2N_2(SO_3K)_2,3H_2O$, formed by heating potassium carbazoledisulphonate with the theoretical amount of dilute nitric acid, crystallises in yellow needles, loses about $2H_2O$ in a desiccator, becomes anhydrous at 160°, intumesces when heated, and dyes wool in an acid-bath a shade resembling naphthol-yellow. Reduction of the nitrodisulphonate by means of hydrogen sulphide in ammoniacal solution leads to the formation of *potassium hydrogen aminocarbazoledisulphonate*,

$$NH_2{\cdot}C_{12}H_6N(SO_3K){\cdot}SO_3H,3H_2O,$$

which crystallises in colourless needles, loses $3H_2O$ at 120°, and when treated with nitrous acid forms a *diazo*-salt; this couples with β-naphthol, forming a red *dye*, which crystallises in needles, and in an acid-bath dyes wool red.

Potassium carbazoletrisulphonate, obtained from the filtrate from the barium disulphonate, crystallises in white needles containing $3H_2O$, which is lost at 190—195°.

Nitration of the product of complete sulphonation of carbazole with excess of concentrated sulphuric acid on the water-bath leads to the formation of a mono- or di-nitrocarbazoledisulphonic acid, depending on the amount of nitric acid employed. The mononitro-acid is obtained in this manner in an almost quantitative yield, and, when reduced and diazotised, couples with β-naphthol, forming a red, or with α-naphthylamine a violet, dye. G. Y.

Derivatives of *p*-Xylidine. GUSTAV SCHULTZ and A. PETENY (*J. pr. Chem.*, 1907, [ii], 76, 331—336).—The base, m. p. 208°, obtained as a by-product in the separation of *p*- and *m*-xylidine by means of benzaldehyde is found to be *phenyldi*-p-*aminodi*-p-*xylylmethane*,

$$CHPh(C_6H_2Me_2{\cdot}NH_2)_2,$$

and is best prepared by boiling benzaldehyde and *p*-xylidine with alcoholic hydrogen chloride. It crystallises in light yellow prisms, and forms a *diacetyl* derivative, $C_{27}H_{30}O_2N_2$, crystallising in white needles, m. p. 217°, and a *dibenzoyl* derivative, $C_{37}H_{34}O_2N_2$, m. p. 249—250°. The action of nitrous acid on the base leads to the formation of a *phenol*, m. p. 162°, which yields a *diacetate*,

$$CHPh(C_6H_2Me_2{\cdot}OAc)_2,$$

crystallising in white needles, m. p. 158°.

Similar bases are obtained by boiling *m*- and *p*-nitrobenzaldehyde with *p*-xylidine and alcoholic hydrogen chloride.

The m-*nitro*-compound, $NO_2{\cdot}C_6H_4{\cdot}CH(C_6H_2Me_2{\cdot}NH_2)_2,C_6H_6$, crystallises from benzene in yellow needles, m. p. 216°, and loses C_6H_6 at 120°, forming orange needles, m. p. 227°. The *diacetyl* derivative, $C_{27}H_{29}O_4N_3$, crystallises in yellow needles, m. p. 232°; the *dibenzoyl* derivative, $C_{37}H_{33}O_4N_3$, crystallises in needles, m. p. 261—262°. The *dihydrochloride* was analysed.

The p-*nitro*-compound crystallises in prisms, m. p. 162°, or after losing C_6H_6 at 120°, m. p. 237°. The *diacetyl* derivative crystallises in white needles, m. p. 192°; the *dibenzoyl* derivative forms yellow needles, m. p. 258—259°; the *dihydrochloride* crystallises in yellow leaflets.

G. Y.

Magnesium Alkylhalides and Carbodi-imides. MAX BUSCH and RICHARD HOBEIN (*Ber.*, 1907, 40, 4296—4298).—Carbodi-imides form additive compounds with magnesium alkylhalides which are decomposed normally by water, forming amidines. Thus carbodiphenylimide and magnesium methyl iodide form colourless needles, m. p. 132°, of diphenylethenylamidine, $NHPh{\cdot}CMe{:}NPh$. *Diphenylbenzenylamidine*, $NHPh{\cdot}CPh{:}NPh$, forms colourless needles, m. p. 144°. Diphenyl-α-naphthenylamidine, $NHPh{\cdot}C(C_{10}H_7){:}NPh$ (Bössneck, Abstr., 1883, 595), forms silky, glistening needles, m. p. 184°; the *hydrochloride* forms transparent, pointed crystals, m. p. 232°. Phenylcyanamide and magnesium phenyl bromide form phenylbenzenylamidine, $NHPh\cdot CPh{:}NH$, colourless needles, m. p. 112°. E. F. A.

Preparation of the Leuco-derivatives of the Indophenols.

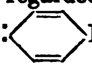
Aktien-Gesellschaft für Anilin-Fabrikation (D.R.-P. 184601, 184651).—When the quinonemonoimines, obtained by oxidation of *p*-aminophenol and its derivatives, are condensed with aromatic bases in dilute hydrochloric acid, leuco-derivatives of the indophenols are produced, providing that the imine is not present in excess.

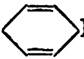
p-Aminophenol hydrochloride, when oxidised in aqueous solution with the calculated amount of ferric chloride, yields quinoneimine, and the addition of a solution of α-naphthylamine hydrochloride leads to the precipitation of leucoindophenol. A similar result is obtained with *o*-chloro-*p*-aminophenol and α-naphthylamine, or the sulphonic acids of this base may be employed.

The leucoindophenols are likewise produced when the phenols, having a free para-position, react with the quinonedi-imines in molecular proportions. Thus *s*-*p*-phenylenedimethyldiamine, oxidised with ferric chloride to quinonedimethylimine and then condensed with phenol in aqueous solutions, furnishes a leucoindophenol which is obtained by salting out. G. T. M.

Tertiary Aromatic Hydrazines and Amines. III.

Heinrich Wieland (*Ber.*, 1907, 40, 4260—4281. Compare Abstr., 1906, i, 453, 830).—The blue or violet coloration obtained when tetraphenylhydrazine is treated with acids (Abstr., 1906, i, 453) is found to be due to the formation of salts of the hydrazine derivative. As tetraphenylhydrazine rapidly undergoes the benzidine rearrangement, the author has investigated the formation of the above salts with tetra-*p*-tolylhydrazine. These violet salts are obtained by the addition, not only of acids, but also of the halogens and of halogen compounds, such as phosphorus pentachloride, thionyl chloride, antimony pentachloride, and stannic, ferric, aluminium, and zinc chlorides. These salts are additive compounds, but not double salts, and are resolved by water or alkali into the tetratolylhydrazine and the decomposition products of the halogen compound employed.

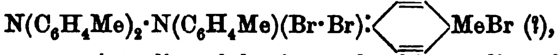
The structure of these additive derivatives is regarded as expressed by the formula: $N(C_6H_4Me)_2\cdot NCl(C_6H_4Me){:}$HMe for the hydrogen chloride compound, and by

$N(C_6H_4Me)_2\cdot N(MCl_n)(C_6H_4Me){:}$$MeCl$

for the other halogen compounds, MCl_n representing PCl_4, $FeCl_2$, &c. This quinonoid constitution is supported by the observation that tetraphenylhydrazine exhibits a tendency to form these additive derivatives much less marked than with tetra-*p*-tolylhydrazine, since, in the case of the simple quinols, the presence of a methyl group in the para-position greatly enhances the stability of the quinol form.

The reduction of these violet salts by stannous chloride yields di-*p*-tolylamine. Their spontaneous decomposition in solution also yields di-*p*-tolylamine together with a pale red compound, which melts at a high temperature, and has the empirical composition of a haloid derivative of di-*p*-tolylamine, although it does not appear to have the simple molecular weight.

The addition of bromine to tetra-*p*-tolylhydrazine results in the formation of a perbromide,

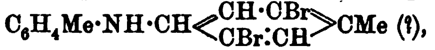


which decomposes into di-*p*-tolylamine and a dibromodi-*p*-tolylamine.

In its unchanged form, tetra-*p*-tolylhydrazine takes up 5 atoms of iodine, yielding a periodide, which has the colour of the associated iodine and shows none of the reactions characterising the violet salts.

Pure, colourless triphenylamine, when added to sulphuric acid either alone or in acetic acid solution, gives no coloration if the liquid is kept cool, but, on heating, an intense, blue coloration appears (compare Goldberg and Nimerovsky, this vol., i, 621); no compound analogous to those formed by tetra-*p*-tolylhydrazine is, however, obtained. Further, tri-*p*-tolylamine does not react with sulphuric, hydrochloric, or acetic acid, but gives with antimony pentachloride, bromine, or phosphorus pentachloride dark blue, crystalline, additive products, which, on decomposition, yield tri-*p*-tolylamine.

The *perbromide* of *tetra-*p*-tolylhydrazine*, $C_{28}H_{28}N_2Br_3$, separates from a benzene-chloroform solution in moderately stable, blackish-violet needles having a faint green, metallic lustre, and decomposes at about 58°. On decomposition, it yields a *dibromodi-*p*-tolylamine*,



$$C_6H_4Me\cdot NH\cdot CH<\begin{matrix}CH\cdot CBr\\ CBr\colon CH\end{matrix}>CMe\ (?),$$

separating from methyl alcohol in colourless, spear-like crystals, m. p. 59°.

The *compound*, $C_{28}H_{28}N_2,PCl_5$, prepared from tetra-*p*-tolylhydrazine and phosphorus pentachloride, separates in slender needles. The *antimony pentachloride* compound, $C_{28}H_{28}N_2,SbCl_5$, forms stable, broad needles with an intense green reflection, m. p. 107° (decomp.); the addition of pyridine to the violet solution causes the gradual disappearance of the colour, whilst the subsequent addition of water precipitates the violet compound. The *periodide*, $C_{28}H_{28}N_2I_5$, crystallises from benzene in shining, blue scales decomposing at 113°.

*Tri-*p*-tolylamine*, $C_{21}H_{21}N$, prepared by the interaction of di-*p*-tolylamine, *p*-iodotoluene, and potassium carbonate in presence of copper (compare Goldberg, Abstr., 1906, i, 426), separates from acetic acid as a faintly yellow, crystalline crust, m. p. 117°, and distils undecomposed; with concentrated sulphuric acid, it gives a colourless solution, which, when heated, assumes a bluish-green colour. With *bromine*, it gives an unstable compound separating in dark blue, bronzy needles, m. p. 40° (decomp.), and giving a dibromotri-*p*-tolylamine, m. p. 160—165°, on decomposition. With phosphorus pentachloride, it forms a *compound*, $C_{21}H_{21}N,PCl_5$, crystallising in dark blue needles, and with antimony pentachloride the *compound*, $C_{21}H_{21}N,SbCl_5$, crystallising in broad, dark blue needles having a metallic lustre, m. p. 116° (decomp.).

T. H. P.

Action of Hydrazine Hydrate on Nitro-compounds. III. Action of Hydrazine Hydrate on 2:4-Dinitrobenzoic Acid. THEODOR CURTIUS and HERMANN F. BOLLENBACH [and, in part, HANS CLEMM] (*J. pr. Chem.*, 1907, [ii], 76, 281—301. Compare this vol., i, 969, 970).—The action of fuming nitric acid on *p*-nitrobenzoic acid leads to the formation of a mixture of 2 : 4- and 3 : 4-dinitrobenzoic acid. 2 : 4-Dinitrobenzoic acid is best prepared by oxidation of 2 : 4-dinitrotoluene with chromic acid in concentrated sulphuric acid solution at 45—50°. *Ethyl* 2 : 4-*dinitrobenzoate*, prepared by boiling the acid with alcoholic hydrogen chloride or by the action of ethyl iodide on the silver salt, crystallises in white needles, m. p. 41°, and readily changes into an oily modification.

2-*Nitro*-4-*aminobenzoic acid*, $C_7H_6O_4N_2$, prepared by boiling 2 : 4-dinitrobenzoic acid with hydrazine hydrate in alcoholic solution, crystallises in scarlet needles, m. p. 255°. The *silver*, $C_7H_5O_4N_2Ag$, and *sodium*, $C_7H_5O_4N_2Na,2H_2O$, salts were analysed. The *ethyl* ester, formed by boiling ethyl 2 : 4-dinitrobenzoate with alcoholic hydrazine hydrate, crystallises in yellow needles, m. p. 130°, and is hydrolysed by boiling dilute sodium hydroxide, forming 2-nitro-4-aminobenzoic acid.

2-*Nitro*-4-*aminobenzoylhydrazide*, $NO_2\cdot C_6H_3(NH_2)\cdot CO\cdot NH\cdot NH_2$, is formed by boiling ethyl 2-nitro-4-aminobenzoate with dilute hydrazine hydrate; it crystallises in golden leaflets or reddish-yellow columns, m. p. 212°, and reduces ammoniacal silver nitrate or Fehling's solution when heated. The *benzylidene* derivative, $C_{14}H_{12}O_3N_4$, forms yellow crystals, m. p. 187—189°; the o-*hydroxybenzylidene* derivative, $C_{14}H_{12}O_4N_4$, separates from alcohol in glistening crystals, m. p. 210°; the iso*propylidene* derivative, $C_{10}H_{12}O_3N_4$, forms golden crystals, m. p. 204—206°. The *dibenzoyl* derivative, $NHBz\cdot C_6H_3(NO_2)\cdot CO\cdot NH\cdot NHBz$, m. p. 239—241°, is prepared by shaking the hydrazide with benzoyl chloride in aqueous sodium hydroxide solution. The *triacetyl* derivative, $C_{13}H_{14}O_6N_4$, obtained by boiling the hydrazide with acetic anhydride, crystallises in leaflets, m. p. 255°.

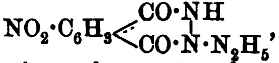
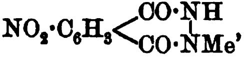
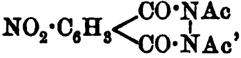
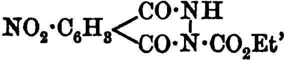
Bis-2-*nitro*-4-*aminobenzoylhydrazide*, $N_2H_2[CO\cdot C_6H_3(NH_2)\cdot NO_2]_2$, formed by boiling the monohydrazide with alcoholic iodine solution or, together with ethyl 2-nitro-4-aminobenzoate, by the action of hydrazine hydrate on ethyl 2 : 4-dinitrobenzoate in ethereal or concentrated alcoholic solution, separates from aqueous alcohol in yellowish-brown crystals, m. p. 238°, and when heated with alcoholic hydrogen chloride at 110° yields hydrazine and 2-nitro-4-aminobenzoic acid.

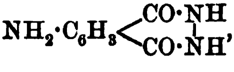
2-*Nitro*-4-*aminobenzoylazoimide*, $NO_2\cdot C_6H_3(NH_2)\cdot CO\cdot N_3$, prepared by the action of sodium nitrite on the hydrazide in acetic acid solution, is obtained as an unstable, red, flocculent precipitate, detonates when heated on platinum, is hydrolysed by dilute sodium hydroxide, forming azoimide and sodium 2-nitro-4-aminobenzoate, and is converted by boiling aniline into 2-*nitro*-4-*aminobenzanilide*, $C_{13}H_{11}O_3N_3$, which crystallises in white needles, m. p. 226°, and forms an *acetyl* derivative, $NHAc\cdot C_6H_3(NO_2)\cdot CO\cdot NHPh$, crystallising in yellow needles, m. p. 238°. The action of boiling alcohol on the azoimide leads to the formation of a dark red syrup, which is probably 2-*nitro*-4-*aminophenylurethane*, $NO_2\cdot C_6H_3(NH_2)\cdot NH\cdot CO_2Et$, since, on successive treatment with an alkali and hydrochloric acid, it yields nitro-*p*-phenylenediamine. When boiled with water, the azoimide forms nitro-*p*-phenylenediamine and *bis-2-nitro-4-aminophenylcarbamide*,

$$CO[NH\cdot C_6H_3(NH_2)\cdot NO_2]_2,$$

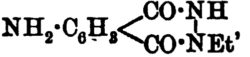
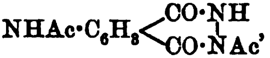
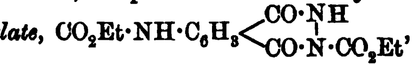
which is hydrolysed by prolonged boiling with concentrated sodium hydroxide, forming nitro-*p*-phenylenediamine.

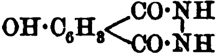
Experimental details as to the action of hydrazine hydrate on nitrobenzene, *m*-dinitrobenzene, nitrophenols, *m*- and *p*-nitrobenzoic acids, and *p*-nitrosodimethylaniline are now given (compare this vol., i, 969). G. Y.

Action of Hydrazine Hydrate on Nitro-compounds. IV. 4-Nitro- and 4-Amino-phthalhydrazides. THEODOR CURTIUS and ALFRED HOESCH (*J. pr. Chem.*, 1907, [ii], 76, 301—330. Compare this vol., 969, 970, and preceding abstract).—When boiled with alcoholic hydrazine hydrate, ethyl 4-nitrophthalate forms *hydrazonium 4-nitrophthalylhydrazide*,  $NO_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot N\cdot N_2H_5\end{matrix}$, which is obtained in yellow and red modifications, does not melt at 300°, forms a red aqueous solution, yields benzaldazine when shaken with aqueous benzaldehyde, and, on treatment with acetic acid, yields 4-nitrophthalylhydrazide (Bogert and Boroschek, Abstr., 1902, i, 98). This is obtained in golden plates, m. p. 298°, sublimes slowly at 200°, has an acid reaction in aqueous solution, and dissolves in aqueous alkalis or alkali carbonates, forming a deep red solution which gives precipitates with salts of the heavy metals. The *potassium*, $C_8H_4O_4N_3K,3H_2O$, *calcium*, $C_{16}H_8O_8N_6Ca$, and *copper*, $C_{16}H_8O_8N_6Cu$, salts are described. The hydrazide remains unchanged when boiled with benzaldehyde or bromine and acetic acid, but yields hydrazine and β-nitrophthalic acid when heated with concentrated hydrochloric acid at 150°. The *methyl* derivative,  $NO_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NMe\end{matrix}$, prepared by heating the potassium salt with methyl iodide at 150°, crystallises in yellow needles, m. p. 295°, and dissolves in aqueous alkalis, forming a red solution. The *diacetyl* derivative,  $NO_2\cdot C_6H_3<\begin{matrix}CO\cdot NAc\\ |\\ CO\cdot NAc\end{matrix}$, obtained by heating the hydrazide with acetic anhydride, forms white leaflets, m. p. 165°, and is hydrolysed by boiling water. *Ethyl 4-nitrophthalylhydrazidecarboxylate*,  $NO_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot N\cdot CO_2Et\end{matrix}$, formed by heating the potassium salt with ethyl chlorocarbonate, crystallises in yellow leaflets, m. p. 115°, and is hydrolysed by boiling water, yielding the hydrazide. The action of ethyl chloroacetate on the potassium salt at 120—150° leads to the formation of a red *powder*, $C_{12}H_{11}O_6N_3$, m. p. 182°. 4-Nitrophthalylhydrazide is attacked by fuming nitric acid at −10°, but not by concentrated nitric acid at the ordinary temperature; the action of potassium permanganate, chromic acid, or potassium dichromate and concentrated sulphuric acid leads to the formation of 4-nitrophthalic acid.

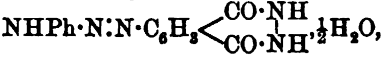
4-Aminophthalylhydrazide,  $NH_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NH\end{matrix}$, prepared by the reduction of the nitro-hydrazide with hydrogen sulphide in ammoniacal solution, or by heating the nitro-hydrazide with an excess of hydrazine hydrate at 130—140°, crystallises in yellow, microscopic needles, does not melt at 300°, has an acid reaction in aqueous solution, is precipitated from its brown alkaline solutions by carbon dioxide, dissolves in hot dilute acids, but separates unchanged on cooling, and gives precipitates with salts of the heavy metals. The *sodium*,

$$C_8H_6O_2N_3Na,7H_2O,$$

calcium, $C_{16}H_{12}O_4N_6Ca$, and *copper*, $C_{16}H_{12}O_4N_6Cu$ and $C_8H_6O_2N_3Cu\cdot OH$, salts are described. When heated with concentrated hydrochloric acid at 150°, the hydrazide is hydrolysed, forming hydrazine and 4-aminophthalic acid; oxidation with nitric acid, permanganate, or dichromate leads to the complete destruction of the molecule. The *ethyl* derivative,  $NH_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ CO\cdot NEt\end{matrix}$, formed from the sodium salt, separates from water in flocculent crystals, m. p. 155°. The *diacetyl* derivative,  $NHAc\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ CO\cdot NAc\end{matrix}$, crystallises in yellow plates, m. p. 212°, and when boiled with water yields a white mixture of the *mono-* and di-acetyl derivatives, m. p. about 270°. *Ethyl 4-aminophthalylhydrazidedicarboxylate*,  $CO_2Et\cdot NH\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ CO\cdot N\cdot CO_2Et\end{matrix}$, crystallises in yellow leaflets, m. p. 148—150°.

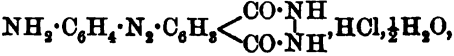
Diazotisation of 4-aminophthalhydrazide with sodium nitrite in sulphuric acid solution leads to the formation of a dark red *solution*, which, when heated on the water-bath, evolves nitrogen, and, on cooling, deposits 4-*hydroxyphthalylhydrazide*,  $OH\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}$; this forms an amorphous, yellow powder, does not melt at 300°, and dissolves in aqueous alkalis or alkali carbonates to a yellowish-red solution. The diazo-sulphate solution couples with resorcinol in alkaline solution, forming a red *dye*, $C_{14}H_{10}O_4N_4$, which in alkaline solution dyes vegetable and animal fibres yellow.

Benzenediazoaminophthalylhydrazide,



$$NHPh\cdot N{:}N\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix},\tfrac{1}{2}H_2O,$$

formed by the action of sodium acetate on a mixture of aniline hydrochloride and diazotised 4-aminophthalylhydrazide in hydrochloric acid solution, is obtained as a yellow precipitate, m. p. 185—187°, and evolves a gas and yields an odour of phenol when heated with dilute acids. p-*Aminobenzene-4-azophthalylhydrazide hydrochloride*,



$$NH_2\cdot C_6H_4\cdot N_2\cdot C_6H_3<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix},HCl,\tfrac{1}{2}H_2O,$$

formed by heating the preceding substance with aniline and aniline hydrochloride, crystallises in dark red prisms, m. p. about 240°, and, when treated with carbon dioxide in ammoniacal solution, yields the free *base*, $C_{14}H_{11}O_2N_5$, which is obtained as an amorphous powder, does not melt at 300°, and is soluble in acids and alkalis. G. Y.

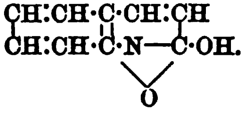
Synthesis of Quinoline Derivatives. IV. Action of Ethyl Benzoylacetate on Anthranilic Acid. STEFAN VON NIEMENTOWSKI (*Ber.*, 1907, 40, 4285—4294. Compare Abstr., 1905, i, 611).—The compound, $C_{30}H_{20}O_5N_2$, m. p. 308° [?318°], described previously (*loc. cit.*) as a by-product of the interaction of ethyl benzoylacetate (1 mol.) and anthranilic acid (1 mol.), is shown to be 4-*anilino-2-hydroxyquinoline*, $C_{15}H_{12}ON_2$, which is obtained in better yield by the action of 2 mols. of anthranilic acid on 1 mol. of the ester. It crystallises from acetone, methyl alcohol ($+ Me{\cdot}OH$), or acetic acid or anhydride ($+ C_2H_4O_2$) in microscopic, six-sided plates, m. p. 318°, and acts as a feeble, monobasic acid. Its *hydrochloride*, $C_{15}H_{12}ON_2,HCl$, forms silky needles, m. p. 160—165°. By the action of fused potassium or sodium hydroxide, or by heating with hydrochloric acid in a sealed tube, 4-anilino-2-hydroxyquinoline is resolved into aniline and 4-hydroxycarbostyril (2 : 4-dihydroxyquinoline). The latter compound, when obtained from its sodium derivative and acetic acid, separates as a crystalline powder, m. p. 340—344°, whilst, after long boiling with nitrobenzene or aniline, it forms stout crystals, m. p. 355°.

When distilled with zinc dust under very low pressure, 4-anilino-2-hydroxyquinoline yields 4-anilinoquinoline (compare Ephraim, Abstr., 1893, i, 727).

2-*Chloro-4-anilinoquinoline*, $C_{15}H_{11}N_2Cl$, obtained by the action of phosphorus pentachloride and oxychloride on 4-anilino-2-hydroxyquinoline, crystallises from alcohol in concentric groups of white needles, m. p. 156°, forms a yellow *hydrochloride*, m. p. 247°, and, when boiled with excess of aniline, yields 2 : 4-dianilinoquinoline (Ephraim, *loc. cit.*), which separates from alcohol in rhombic crystals.

The mechanism of the formation of 4-anilino-2-hydroxyquinoline is probably as follows. One of the two mols. of anthranilic acid is resolved into carbon dioxide and aniline, the latter then immediately reacting with the second mol. of anthranilic acid giving aminobenzoylanilide. This then reacts either with ethyl benzoylacetate yielding 4-anilino-2-hydroxy-3-benzoylquinoline, the benzoyl group of which is removed by hydrolysis, or with ethyl acetate, a product of the decomposition of ethyl benzoylacetate, giving 4-anilino-2-hydroxyquinoline directly.

The compound, $C_9H_7O_2N$, termed hydroxycarbostyril by Friedländer and Ostermaier (Abstr., 1882, 201, 732), and obtained together with carbostyril by reducing ethyl *o*-nitrocinnamate with alcoholic ammonium sulphide, is regarded by the author as having the constitution:



$$\begin{array}{l} CH{:}CH{\cdot}C{\cdot}CH{:}CH \\ CH{:}CH{\cdot}C{\cdot}N{-}C{\cdot}OH. \\ \qquad\qquad\quad O \end{array}$$

T. H. P.

Preparation of 5-Hydroxy-3′-aminophenyl-1 : 2-naphthiminazoledisulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 186883).—5-*Hydroxy*-3′-*aminophenyl*-1 : 2-*naphthiminazole*-7-?-*disulphonic acid* is an almost colourless, sparingly soluble compound, obtained by sulphonating 5-hydroxy-3′-aminophenyl-1 : 2-naphthiminazole-7-sulphonic acid on the water-bath with fuming sulphuric acid (25% SO_3). Its alkali salts are readily soluble, as are also those of barium, strontium, and calcium ; the yellow copper salt dissolves in water only sparingly. G. T. M.

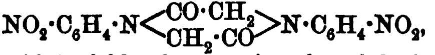
2 : 5-Diketo-dinitro- and -diamino-diphenylpiperazines. E. DEUTSCH (*J. pr. Chem.*, 1907, [ii], 76, 350—363).—m-*Nitrophenylglycine*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, prepared by heating *m*-nitroaniline with chloroacetic acid in sodium acetate and carbonate solution, crystallises in doubly refracting, yellow, rhombic prisms, m. p. 156° (corr.), decomp. slightly above its m. p., and dissolves in aqueous sodium carbonate or acetate. The *ethyl* ester,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et,$$

prepared from *m*-nitroaniline and ethyl chloroacetate, forms pleochroic crystals, m. p. 84° (corr.).

Chloroacetyl-*m*-nitroanilide (Johnson and Cramer, Abstr., 1903, i, 581) crystallises in doubly refracting plates, m. p. 116° (corr.), decomp. 150—160°, and is hydrolysed by alcoholic potassium hydroxide, forming *m*-nitroaniline together with traces of the *m*-nitroanilide of glycollic acid if in presence of water.

2 : 5-*Diketodi*-m-*nitrodiphenylpiperazine*,

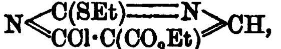
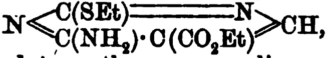


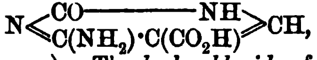
$$NO_2{\cdot}C_6H_4{\cdot}N{<}\begin{matrix}CO{\cdot}CH_2\\CH_2{\cdot}CO\end{matrix}{>}N{\cdot}C_6H_4{\cdot}NO_2,$$

is obtained in a 20% yield when *m*-nitrophenylglycine, or in a 10% yield when chloroacetyl-*m*-nitroanilide, is heated at 160—170°; it forms a yellow, crystalline powder, m. p. 157° (corr.), and is hydrolysed to *m*-nitrophenylglycine by alcoholic potassium hydroxide.

The action of chloroacetyl chloride on *m*-nitrophenylglycine leads to the formation of *chloroacetyl*-m-*nitrophenylglycine*, which cannot be obtained free from unchanged *m*-nitrophenylglycine; when boiled with excess of *m*-nitroaniline in benzene, it forms small amounts of 2 : 5-diketodi-*m*-nitrodiphenylpiperazine. Reduction of this with tin and hydrochloric acid leads to the formation of 2 : 5-*diketo-di*-m-*aminodiphenylpiperazine dihydrochloride*, $C_{16}H_{18}O_2N_4Cl_2$, which is obtained in colourless, doubly refracting crystals. The free *base* is colourless, but on exposure to air rapidly becomes yellow, changing to green and black. Orange-red to yellow *dyes*, which dye wool, but not cotton, are obtained by coupling the diazotised base with R-salt and salicylic acid.

Chloroacetyl-p-*nitroanilide* crystallises in doubly refracting plates, m. p. 152° (corr.), and resembles the *m*-nitroanilide in its behaviour to hydrolysing agents. When heated at 170°, it yields 2 : 5-*diketodi*-p-*nitrodiphenylpiperazine*, $C_{16}H_{12}O_6N_4$, which is obtained as a yellow powder, m. p. 147° (corr.), and when boiled with alcoholic potassium hydroxide is hydrolysed to *p*-nitrophenylglycine. The *dihydrochloride*, obtained on reduction of the di-*p*-nitro-compound in hydrochloric acid solution, forms colourless, doubly refracting prisms; the free *base* is colourless, rapidly darkens on exposure to air, and, when diazotised and coupled with R-salt and salicylic acid, yields *dyes* which dye wool, but not cotton, a dirty, brown yellow. G. Y.

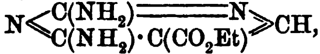
Pyrimidines. XXVI. Synthesis of Cytosine-5-carboxylic Acid. HENRY L. WHEELER and CARL O. JOHNS (*Amer. Chem. J.*, 1907, 38, 594—602).—When ethyl 2-ethylthiol-6-oxypyrimidine-5-carboxylate (Wheeler, Johnson, and Johns, this vol., i, 559) is boiled with phosphorus oxychloride, it is converted into *ethyl 6-chloro-2-ethylthiolpyrimidine-5-carboxylate*,  $\mathrm{N}\left<\begin{matrix}\mathrm{C(SEt)}=\!=\!=\!=\mathrm{N}\\ \mathrm{CCl\cdot C(CO_2Et)}\end{matrix}\right>\mathrm{CH}$, b. p. 203°/20 mm. This substance, on treatment with cold alcoholic ammonia, yields *ethyl 6-amino-2-ethylthiolpyrimidine-5-carboxylate*,  $\mathrm{N}\left<\begin{matrix}\mathrm{C(SEt)}=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C(NH_2)\cdot C(CO_2Et)}\end{matrix}\right>\mathrm{CH}$, m. p. 102°, which forms rectangular plates; the corresponding *acid*, m. p. 230° (decomp.), crystallises in microscopic prisms, and when heated with concentrated hydrochloric acid is converted into *cytosine-5-carboxylic acid*,



$$\mathrm{N}\left<\begin{matrix}\mathrm{CO}\text{———————}\mathrm{NH}\\ \mathrm{C(NH_2)\cdot C(CO_2H)}\end{matrix}\right>\mathrm{CH},$$

m. p. 256—257° (decomp.). The *hydrochloride* of cytosine-5-carboxylic acid, m. p. 275—276°, forms pointed prisms containing $1H_2O$. The *ethyl* ester crystallises in needles, and decomposes slowly at 260—275°. The *amide* forms tufts of hair-like needles. When cytosine-5-carboxylic acid is heated with 20% sulphuric acid, it yields uracil-5-carboxylic acid (*loc. cit.*) together with a small quantity of cytosine. These results indicate that cytosine does not exist in the nucleic acids in the form of a 5-carboxyl derivative.

Ethyl 2 : 6-*diaminopyrimidine-5-carboxylate*,

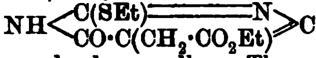


$$\mathrm{N}\left<\begin{matrix}\mathrm{C(NH_2)}=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{C(NH_2)\cdot C(CO_2Et)}\end{matrix}\right>\mathrm{CH},$$

m. p. 205—207°, obtained by heating ethyl 6-amino-2-ethylthiolpyrimidine-5-carboxylate with alcoholic ammonia at 168—178°, crystallises in needles.

E. G.

Pyrimidines. XXVII. Synthesis of Thymine-5′-carboxylic Acid. TREAT B. JOHNSON and CARL FRANK SPEH (*Amer. Chem. J.*, 1907, 38, 602—613).—The study of the carboxylic acids of uracil, cytosine, and thymine has been undertaken with a view to obtain evidence as to whether these bases are linked in nucleic acid by means of an acid amide group (compare Wheeler, Johnson, and Johns, this vol., i, 559, and preceding abstract; Johnson, this vol., i, 879, and Wheeler, this vol., i, 972). The results so far obtained indicate that uracil is the only one of these pyrimidines which is capable of being united in this way and that this might exist as a 5-carboxyl compound.

Ethyl formylsuccinate, $CO_2Et\cdot CH(CHO)\cdot CH_2\cdot CO_2Et$, b. p. 158—160°/20 mm., is obtained by the condensation of ethyl formate and succinate in presence of sodium. By the action of its sodium derivative on ψ-ethylthiocarbamide, *ethyl 6-oxy-2-ethylthiolpyrimidine-5-acetate*,  $\mathrm{NH}\left<\begin{matrix}\mathrm{C(SEt)}=\!=\!=\!=\!=\!=\mathrm{N}\\ \mathrm{CO\cdot C(CH_2\cdot CO_2Et)}\end{matrix}\right>\mathrm{CH}$, m. p. 146—147°, is produced which forms slender needles. The corresponding *acid*, m. p. 184°, crystallises in needles and square plates; its *potassium* salt forms long needles.

By the action of phosphorus oxychloride on ethyl 6-oxy-2-ethylthiolpyrimidine-5-acetate, 6-*chloro-2-ethylthiolpyrimidine-5-acetic acid*, $N{<}\begin{array}{l}C(SEt)=\!=\!=\!=\!=N\\ CCl\cdot C(CH_2\cdot CO_2H)\end{array}{>}CH$, m. p. 132°, is produced and forms clusters of prismatic crystals. The corresponding *amide*, m. p. 214° (decomp.), obtained by heating ethyl 6-oxy-2-ethylthiolpyrimidine-5-acetate with alcoholic ammonia at 140—150°, crystallises in prismatic needles; if the mixture is heated at 170—180°, 2-*amino-6-oxypyrimidine-5-acetamide*, $NH{<}\begin{array}{l}C(NH_2)=\!=\!=\!=\!=N\\ CO\cdot C(CH_2\cdot CO\cdot NH_2)\end{array}{>}CH$, is produced, which forms prismatic crystals and decomposes at about 280°.

Thymine-ω-carboxylic acid, $NH{<}\begin{array}{l}CO\text{———————}NH\\ CO\cdot C(CH_2\cdot CO_2H)\end{array}{>}CH$, m. p. 315—320° (decomp.), obtained by the action of hydrochloric acid on ethyl 2-ethylthiol-6-oxypyrimidine-5-acetate, forms microscopic, granular crystals, dissolves to the extent of 0·35—0·40 part in 100 parts of water at 30°, reddens blue litmus, and yields a precipitate with solutions of silver nitrate or mercuric chloride. The *potassium* and *lead* salts are described. The *ethyl* ester, m. p. 204—210°, forms rectangular plates. The acid can be heated with 20% sulphuric acid without change, and it therefore follows that thymine cannot exist in nucleic acids as a ω-carboxyl compound. E. G.

Preparation of 5 : 5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 180669. Compare Abstr., 1905, i, 671).—The 2 : 4-di-imino-6-oxy-5 : 5-dialkylpyrimidines when heated with mineral acids readily lose their two imino-groups and yield the corresponding 5 : 5-dialkylbarbituric acids. In this way, 2 : 4-di-imino-6-oxy-5 : 5-diethylpyrimidine gives rise to 5 : 5-diethylbarbituric acid, and 2 : 4-di-imino-6-oxy-5 : 5-dimethylpyrimidine furnishes 5 : 5-*dimethylbarbituric acid*, small leaflets, m. p. 267°. G. T. M.

Pyrazolone Derivatives. RUDOLF KOBERT (*Chem. Zentr.*, 1907, i, 1804—1805; from *Zeitsch. klin. Med.*, 1907, 62, 1—43. Compare Michaelis, this vol., i, 246).—The behaviour of antipyrine, 3-antipyrine, *iso*antipyrine, nitroso- and amino-antipyrines, pyramidone, 3-pyramidone, pyramidone methiodide, *iso*pyramidone, and thiopyrine towards several reagents is given in the original. The physiological action of several of these compounds has also been investigated. Toxicity decreases in the order: 3-antipyrine, *iso*antipyrine, antipyrine, and aminoantipyrine. Pyramidone is more poisonous than *iso*pyramidone, 3-pyramidone, 3-pyramidone methiodide, and aminoantipyrine. Azoantipyrine and 4-alkylantipyrine are also very poisonous.

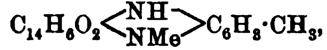
W. H. G.

Colouring Matters of the Indanthrene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 178130).—The 1 : 2- and 2 : 3-diaminoanthraquinones condense with alizarin and its derivatives to yield indanthrene colouring matters containing two anthraquinone residues; the condensation being generally effected by heating the reagents in boiling phenol or cresol in the presence of boric acid. The indanthrene obtained from 1 : 2-diaminoanthraquinone and alizarin has the formula: $C_6H_4<{CO \atop CO}>C_6H_4<{NH \atop NH}>C_6H_4<{CO \atop CO}>C_6H_4$, and is probably isomeric with the indanthrene of commerce.

Purpurin and 1 : 2-diaminoanthraquinone gives rise to hydroxyindanthrene, which, on reduction, yields a blue vat-dye and gives greenish-blue shades on unmordanted cotton. The patent contains a tabulated description of nine of these indanthrene derivatives.

G. T. M.

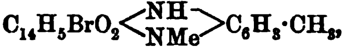
[Preparation of Azines Derived from Anthraquinone.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 184391).—When the aldehydes react with the aryl-*o*-diaminoanthraquinones, new coloured substances are produced, which are regarded as azine derivatives. 2-Amino-1-*p*-tolylaminoanthraquinone, when condensed with formaldehyde solution (40%) in glacial acetic acid at 100°, furnishes *anthraquinonyl*-N-*methyldihydro*-p-*toluazine*,



$$C_{14}H_6O_2<{NH \atop NMe}>C_6H_3\cdot CH_3,$$

which separates as a blue, crystalline precipitate.

3-*Bromoanthraquinonyl*-N-*methyldihydro*-p-*toluazine*,



$$C_{14}H_5BrO_2<{NH \atop NMe}>C_6H_3\cdot CH_3,$$

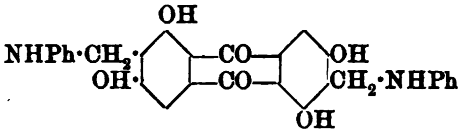
blue needles, is prepared in a similar manner from 3-bromo-2-amino-1-p-tolylaminoanthraquinone. The properties of these and seven other complex dihydro-azines are tabulated in the patent. The sulphonic acids of all these substances are wool dyes, giving various shades of blue.

G. T. M.

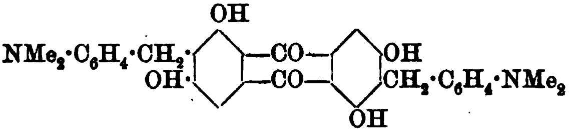
[Preparation of 2′ : 2′-Dianthraquinonyl-1 : 5-diaminoanthraquinone.] Badische Anilin- und Soda-Fabrik (D.R.-P. 184905).—When 1 : 5-diaminoanthraquinone is heated to boiling in naphthalene or nitrobenzene solution with 2-chloroanthraquinone in the presence of dry sodium acetate and cupric or cuprous chloride, 2 : 2-*dianthraquinonyl*-1 : 5-*diaminoanthraquinone*, $C_{10}H_6O_2(NH\cdot C_{10}H_7O_2)_2$, is produced as a compound insoluble in the organic media; it dissolves in concentrated sulphuric acid to a green solution, and is reduced by alkaline hyposulphite to give a vat-dye producing very fast shades of red on cotton.

G. T. M.

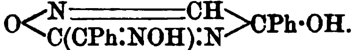
[Preparation of *ω*-Dianilinodimethyltetrahydroxyanthraquinone and *pp*-Tetramethyldiaminodibenzyltetrahydroxyanthraquinone.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 184807, 184808).—The condensation product from anthrachrysone (tetrahydroanthraquinone) and formaldehyde, when heated with excess of aniline so long as steam is evolved, gives rise to *ω*-*dianilino*-2 : 4 : 6 : 8-*tetrahydroxy*-3 : 7-*dimethylanthraquinone*, separating from the cooled



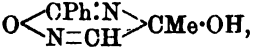
solution in orange-yellow crystals, which on heating decompose without definite melting point. Corresponding compounds may be obtained with the toluidines and xylidines. pp-*Tetramethyldiamino*-2 : 4 : 6 : 8-*tetrahydroxy*-3 : 7-*dibenzylanthraquinone*, produced by substituting dimethylaniline for aniline in the foregoing condensation, separates in orange-yellow crystals, m. p. 272°. The corresponding tetraethyl derivative melts at 233°.



G. T. M.

Oxadiazines. II. Otto Diels and Erich Sasse (*Ber.*, 1907, **40**, 4052—4059. Compare Abstr., 1905, i, 946).—*iso*Nitrosoacetone and *iso*nitrosoacetophenone react like diacetylmonoxime with *syn.*-benzaldoxime hydrochloride forming oxadiazines. In the presence of anhydrous hydrogen chloride, the *iso*nitroso-compound reacts with itself (or with its isomeric modification) yielding an oxadiazine containing a carbonyl group, from which an oxime is readily obtained. Thus from *iso*nitrosoacetophenone is obtained an oxime of the formula $C_{16}H_{13}O_3N_3$, which appears to be identical with a substance prepared by Müller and von Pechmann (Abstr., 1890, 51) and by Scholl (Abstr., 1891, 287). The latter regarded the substance as the dioxime of 5-benzoyl-3-phenyl-4-*iso*oxazolone. The author brings forward evidence to show that the preparation and properties of the substance harmonise better with the oxadiazine formula,  $O\Big<\begin{matrix}N\text{=======}CH\\C(CPh{:}NOH){:}N\end{matrix}\Big>CPh\cdot OH$.

4-*Hydroxy*-6-*phenyl*-4-*methyl*-1 : 2 : 5-*oxadiazine*,


$$O\Big<\begin{matrix}CPh{:}N\\N{=}CH\end{matrix}\Big>CMe\cdot OH,$$

darkens at 170—180° and decomposes at 220—225°; the *methiodide*, $C_{12}H_{15}O_2N_2I_3$, has m. p. 108—109°. The *hydrochloride*,

$$C_{10}H_{10}O_2N_2,HCl,$$

m. p. 137—138°, softening at 134—135°, is prepared from *iso*nitrosoacetone and *syn.*-benzaldoxime hydrochloride in methyl-alcoholic solution; with boiling water, it yields the preceding base.

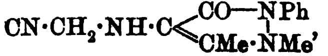
4-*Hydroxy*-6-*benzoyl*-4-*phenyl*-1 : 2 : 5-*oxadiazine hydrochloride*,

$$C_{16}H_{12}O_3N_2,HCl,$$

is obtained by passing a rapid current of hydrogen chloride through an ethereal solution of *iso*nitrosoacetophenone; it separates in stout, yellow, prismatic needles, which decompose violently at 215°. Boiling water liberates the *base*, $C_{16}H_{12}O_3N_2$, m. p. 220—226°, which forms a yellow, crystalline *sodium* salt, which decomposes at 215°, and the oxime, which decomposes at 221—222° (Müller and von Pechmann, m. p. 219°; Scholl, m. p. 207—211°).

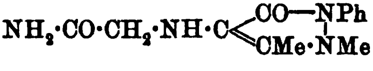
C. S.

Preparation of 4-Antipyryldimethylamine. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 184850).—4-*Cyanomethylamino*-1-*phenyl*-2 : 3-*dimethylpyrazolone* (4-*antipyrylcyanomethylamine*),


$CN\cdot CH_2\cdot NH\cdot C\Big<\begin{matrix}CO\text{—}NPh\\CMe\cdot NMe\end{matrix}$, colourless leaflets, m. p. 112°, is pro-

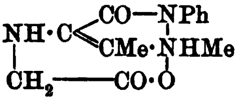
duced by treating an aqueous solution of 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone successively with formaldehyde, sodium hydrogen sulphite, and potassium cyanide, when it separates as an oil which becomes solid on cooling; it dissolves only sparingly in ether, but is readily soluble in hot water or benzene, or in cold alcohol or chloroform.

4-*Antipyrylaminoacetamide* (I), m. p. 194°, colourless prisms from alcohol or water, is obtained on boiling the preceding cyano-



$$NH_2\cdot CO\cdot CH_2\cdot NH\cdot C{<}\begin{matrix}CO-NPh\\ CMe\cdot NMe\end{matrix}$$

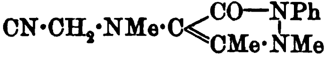
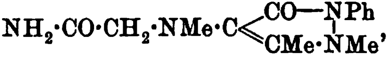
(I.)



$$\begin{matrix}NH\cdot C{<}\begin{matrix}CO-NPh\\ CMe\cdot NHMe\end{matrix}\\ CH_2-\!\!-\!\!-CO\cdot O\end{matrix}$$

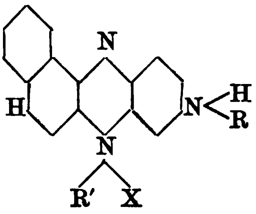
(II.)

compound with water, or on leaving it in contact with concentrated hydrochloric acid. On boiling either of the preceding compounds with concentrated hydrochloric acid, the betaine (II) is produced, which is only sparingly soluble in all organic media, and crystallises from alcohol in lustrous needles, m. p. above 300°.

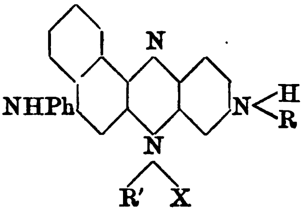
4-*Antipyrylcyanodimethylamine*,  $CN\cdot CH_2\cdot NMe\cdot C{<}\begin{matrix}CO-NPh\\ CMe\cdot NMe\end{matrix}$, colourless crystals, m. p. 75°, is prepared by alkylating 4-antipyrylcyanomethylamine with methyl iodide in methyl-alcoholic solution. 4-*Antipyrylmethylaminoacetamide*,  $NH_2\cdot CO\cdot CH_2\cdot NMe\cdot C{<}\begin{matrix}CO-NPh\\ CMe\cdot NMe\end{matrix}$, leaflets from benzene, m. p. 158—159°, is similarly obtained by methylating 4-antipyrylaminoacetamide. 4-*Antipyrylmethylaminoacetic acid*, prepared by methylating the foregoing betaine, is a very soluble substance, having a hygroscopic sodium salt soluble in chloroform.

The last three compounds can be hydrolysed so as to yield the therapeutically important 4-antipyryldimethylamine. G. T. M.

[Preparation of Naphthaphenosafranine Derivatives.] **Friedrich Kehrmann** (D.R.-P. 183117).—The *iso*rosinduline salts of the general type (I; where X is the acid ion) have the



(I.)



(II.)

hydrogen atom, indicated in the naphthalene residue, replaced by the group NHR″ when the colouring matter is treated with an amine in the presence of an oxidising agent, such as atmospheric air. Condensation with aniline would lead to the formation of substances indicated by the general formula (II).

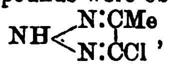
Ethyl*iso*rosinduline chloride, obtained from nitrosoethylaniline and phenyl-β-naphthylamine when treated with aniline and aqueous sodium hydroxide at 80—90° while a current of air is passed through the mixture, gives rise to a colour base separating in green crystals with a metallic lustre. Phenyl*iso*rosinduline chloride and *p*-aminoacetanilide yield a similar product, which separates in golden-yellow crystals. Sulphonation and hydrolysis of the acetyl group lead to the production of a soluble sulphonic dye. Phenyl*iso*rosinduline disulphonic acid furnishes similar condensation products on treatment with aromatic amines and sodium hydroxide. G. T. M.

Action of Diazo-derivatives of Aliphatic Hydrocarbons on Cyanogen and its Derivatives. III. Halogenated Compounds.

ANTONIO TAMBURELLO and A. MILAZZO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 412—418. Compare Peratoner and Azzarello, this vol., i, 979).—The action of cyanogen chloride or bromide on diazomethane or diazoethane in ethereal solution yields a chloro-derivative of osotriazole, which usually undergoes subsequent etherification by the diazo-compound:

$CH_2<\begin{array}{l}N\\ \|\\ N\end{array} + CNCl = NH<\begin{array}{l}N:CH\\ N:CCl\end{array}$, and $NH<\begin{array}{l}N:CH\\ N:CCl\end{array} + CH_2N_2$

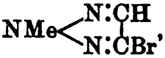
$= N_2 + NMe<\begin{array}{l}N:CH\\ N:CCl\end{array}$; cyanogen chloride gives the best yields, whilst with the iodide no definite compounds were obtained.

4-*Chloro*-3-*methylosotriazole*,  $NH<\begin{array}{l}N:CMe\\ N:CCl\end{array}$, prepared from cyanogen chloride and diazoethane, crystallises from benzene in shining, white needles, m. p. 77—78°.

4-*Chloro*-3-*methyl*-1-*ethylosotriazole*, $NEt<\begin{array}{l}N:CMe\\ N:CCl\end{array}$, is a colourless liquid, b. p. 86—88°/40 mm., which has a pleasing odour and is insoluble in water.

4-*Bromo*-3-*methyl*-1-*ethyltriazole*, $C_5H_8N_3Br$, is a colourless liquid, b. p. 84—85°/30 mm., having a pleasant odour.

3-*Chloro*-1-*methylosotriazole*, $NMe<\begin{array}{l}N:CH\\ N:CCl\end{array}$, is a colourless liquid, b. p. 62—65°/39 mm., having a pleasant odour.

3-*Bromo*-1-*methylosotriazole*,  $NMe<\begin{array}{l}N:CH\\ N:CBr\end{array}$, is a colourless liquid, b. p. 62—65°/22 mm., and has a pungent odour which excites to tears.

T. H. P.

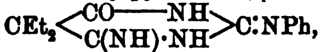
Preparation of 2-Alkyliminopyrimidines.

EMANUEL MERCK (D.R.-P. 186456).—The 2-alkyliminopyrimidines,

$$CEt_2<\begin{array}{l}CO{\cdot}NH\\ CO{\cdot}NH\end{array}>C:NX$$

(where X is an alkyl or aryl group), were obtained by condensing the corresponding guanidine, $NX:C(NH_2)_2$, with malonyl halides, alkyl malonamates, alkyl cyanoacetates, or their mono- and di-alkyl derivatives.

Phenylguanidine and ethyl cyanodiethylacetate give rise to 4-imino-6-oxy-2-phenylimino-5 : 5-diethylpyrimidine,



$$CEt_2\left<\begin{array}{l}CO\text{——}NH\\C(NH)\cdot NH\end{array}\right>C:NPh,$$

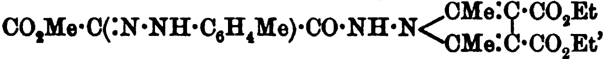
which is readily hydrolysed to 5 : 5-diethylbarbituric acid.

4-*Imino*-6-*oxy*-2-*phenyliminopyrimidine*, m. p. 244°, was produced by condensing phenylguanidine and ethyl cyanoacetate with alcoholic sodium ethoxide. 4-*Imino*-6-*oxy*-2-*methylimino*-5 : 5-*diethylpyrimidine*, m. p. 265°, was obtained from methylguanidine and ethyl cyanodiethylacetate. 4 : 6-*Dioxy*-2-*phenylimino*-5 : 5-*diethylpyrimidine*, needles, m. p. 255°, was prepared from phenylguanidine and diethylmalonyl chloride. G. T. M.

Derivatives of Methyl Mesoxalate-*p*-tolylhydrazone. Carl Bülow and Richard Weidlich (*Ber.*, 1907, **40**, 4326—4332. Compare Abstr., 1906, i, 981).—Methyl mesoxalate-*p*-tolylhydrazone (Bülow and Ganghofer, Abstr., 1905, i, 90) in cold alcoholic solution reacts with 50% hydrazine hydrate to form the *hydrazide*,

$$CO_2Me\cdot C(:N\cdot NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot NH_2,$$

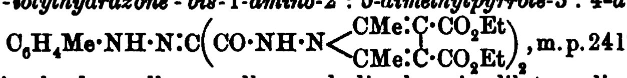
m. p. 160°, which separates from dilute alcohol in slender, yellow needles, and is converted by acetic anhydride into the *acetyl* derivative, $CO_2Me\cdot C(:N\cdot NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot NHAc$, m. p. 186°. The hydrazide condenses with benzaldehyde in boiling alcohol to form the *benzylidene* compound, $CO_2Me\cdot C(:N\cdot NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot N:CHPh$, m. p. 163°, and with acetone, yielding the corresponding iso*propylidene* compound, $CO_2Me\cdot C(:N\cdot NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot N:CMe_2$, m. p, 165°. The hydrazide and ethyl diacetylsuccinate in very slightly diluted glacial acetic acid form *methyl diethyl mesoxalyl*-p-*tolylhydrazone*-1-*amino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,



$$CO_2Me\cdot C(:N\cdot NH\cdot C_6H_4Me)\cdot CO\cdot NH\cdot N\left<\begin{array}{l}CMe:C\cdot CO_2Et\\CMe:C\cdot CO_2Et\end{array}\right.,$$

m. p. 161—162°, which separates from dilute alcohol in stout, yellow needles.

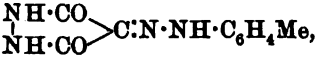
The *dihydrazide*, $C_6H_4Me\cdot NH\cdot N:C(CO\cdot NH\cdot NH_2)_2$, m. p. 196°, is obtained by heating the mother liquor of the monohydrazide for five hours on the water-bath, or the calculated quantities of 50% hydrazine hydrate and methyl mesoxalate-*p*-tolylhydrazone for four hours; the *acetyl* derivative, $C_{14}H_{18}O_4N_6$, m. p. 247°, is a yellow powder. *Ethyl mesoxalyl*-p-*tolylhydrazone*-*bis*-1-*amino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,



$$C_6H_4Me\cdot NH\cdot N:C\left(CO\cdot NH\cdot N\left<\begin{array}{l}CMe:C\cdot CO_2Et\\CMe:C\cdot CO_2Et\end{array}\right.\right)_2,$$

m. p. 241°, crystallises in slender, yellow needles, and dissolves in dilute sodium hydroxide.

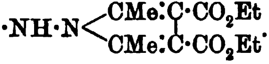
3 : 5-*Pyrazolidone*-4-p-*tolylhydrazone*,



$$\begin{array}{l}NH\cdot CO\\NH\cdot CO\end{array}\!\!>C:N\cdot NH\cdot C_6H_4Me,$$

m. p. 267°, is prepared by passing carbon dioxide through the mother liquor of the dihydrazide or through the cold filtrate obtained after heating methyl mesoxalate-*p*-tolylhydrazone and a slight excess of hydrazine hydrate in alcohol for twelve hours. In alkaline solution, it reacts with methyl sulphate to form 1 : 2-*dimethyl*-3 : 5-*pyrazolidone*-4-p-*tolylhydrazone*, m. p. 170°, which crystallises in red needles.

The authors formulate the rule : hydrazides of organic acids react with ethyl diacetylsuccinate in acetic acid solution to form compounds in which the hydroxyl group of the acid is replaced by the complex :



$$\cdot\mathrm{NH}\cdot\mathrm{N}<\begin{array}{l}\mathrm{CMe{:}C\cdot CO_2Et}\\ \mathrm{CMe{:}C\cdot CO_2Et}\end{array}.$$

C. S.

[Diazotisation of Acetyl-2 : 6-diaminophenol-4-sulphonic Acid.] Kalle & Co. (D.R.-P. 182853).—6-Nitro-2-acetylaminophenol-4-sulphonic acid is reduced without losing its acetyl group or undergoing condensation by means of iron filings and water acidified with acetic acid. The resulting acetyl-2 : 6-diaminophenol-4-sulphonic acid yields a very stable diazo-compound, which when warmed at 40—45° for six hours with dilute hydrochloric acid loses its acetyl group, whilst the diazo-complex remains intact. G. T. M.

Transformations of Azo-compounds into Hydrazones. Otto Dimroth and Max Hartmann (*Ber.*, 1907, **40**, 4460—4465).—Benzeneazo- and *p*-bromobenzeneazo-acetyldibenzoylmethane and *p*-bromobenzeneazotribenzoylmethane behave in the same manner as *p*-nitrobenzeneazoacetyldibenzoylmethane (this vol., i, 662), changing into colourless isomerides when heated alone or with indifferent solvents. The coloured substances are azo-compounds, $\mathrm{NR{:}N\cdot C(COR')_2\cdot COR''}$, whilst the colourless isomerides are hydrazones, $\mathrm{COR''\cdot NR\cdot N{:}C(COR')_2}$, which do not undergo the converse transformation in benzene, ether, or chloroform at 160°.

Benzeneazoacetyldibenzoylmethane, $C_{23}H_{18}O_3N_2$, prepared by addition of diazobenzene chloride and sodium acetate to the enolic modification of acetyldibenzoylmethane in alcoholic solution at 0°, forms yellow crystals, m. p. 90°, evolving gas. The isomeric *hydrazone* crystallises in white needles, m. p. 188°.

p-*Bromobenzeneazoacetyldibenzoylmethane*, $C_{23}H_{17}O_3N_2Br$, forms amber-coloured, monoclinic crystals, m. p. 113°. The *hydrazone*, $\mathrm{C_6H_4Br\cdot NAc\cdot N{:}C(COPh)_2}$, crystallises in white needles, m. p. 218°, and when reduced with zinc dust and ammonia yields acet-*p*-bromoanilide. On treatment with sodium ethoxide at 0°, both isomerides yield p-*bromobenzeneazodibenzoylmethane*, $C_{21}H_{15}O_2N_2Br$, crystallising in golden leaflets, m. p. 147—149°.

p-*Bromobenzeneazotribenzoylmethane*, $C_{28}H_{19}O_3N_2Br$, forms yellow crystals, m. p. 130—135°. The *hydrazone* crystallises in colourless needles, m. p. 220—221°, and is reduced by zinc dust and acetic acid, forming benzo-*p*-bromoanilide. G. Y.

[Combination of *o*-Diazo-oxides with 1 : 8-Dihydroxynaphthalene-3 : 6-disulphonic Acid.] Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P. 184689).—The nitro-*o*-aminophenols, containing the nitro-group in the para-position with respect to the amino-group, yield sparingly soluble, yellow diazo-oxides, which couple far more readily with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromotropic acid) in the presence of calcium hydroxide than when sodium hydroxide or carbonate is employed. The azo-sulphonic acids thus produced give various shades of blue on chrome-mordanted wool.

G. T. M.

Etherification of Hydroxyazo-compounds by means of Methyl Sulphate. AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 457—464).—As a rule, hydroxyazo-compounds can be converted quantitatively into the corresponding methoxyazo-derivatives by shaking their alkaline solutions for a short time with a slight excess of methyl sulphate. In some cases, for example, with azo-compounds derived from phenols in which the para-position is occupied by another radicle, the etherification is only effected on heating, and proceeds best when an absolute alcoholic solution of the alkali derivative of the hydroxyazo-compound is treated with methyl sulphate.

This method has been applied to the preparation of the methyl ethers of benzeneazophenol, 2 : 4 - bisbenzeneazophenol, benzeneazoguaiacol, m. p. 53—54° [Jacobson, Jaenicke, and Meyer gave m. p. 44·5—45° (Abstr., 1897, i, 143)], and the following new compounds.

The *methyl ether* of o-*nitrobenzeneazoguaiacol*, $C_{14}H_{13}O_4N_3$, separates from alcohol in reddish-brown crystals, m. p. 152°.

The *methyl ether* of *β-naphthylazoguaiacol*, $C_{18}H_{16}O_2N_2$, is deposited from alcohol in long, orange-red, acicular crystals, m. p. 103—105°.

The *methyl ether* of p-*bromobenzeneazoeugenol*, $C_{17}H_{17}O_2N_2Br$, separates from benzene in minute, pale-yellow crystals, m. p. 92—94°.

The *methyl ether* of m-*xyleneazoeugenol*, $C_{19}H_{22}O_2N_2$, forms minute, brick-red crystals, m. p. 56°.

T. H. P.

Esterification of Azo-derivatives of Hydroxy-acids by means of Methyl Sulphate. AMEDEO COLOMBANO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 547—551. Compare preceding abstract).—When an azo-derivative of *o*- or *m*-hydroxybenzoic acid is treated with rather more than 2 mols. of potassium hydroxide and rather more than 2 mols. of methyl sulphate, it yields a mixture of the esters: $N_2R\cdot C_6H_3(OH)\cdot CO_2Me$ and $N_2R\cdot C_6H_3(OMe)\cdot CO_2Me$. In the cases examined, the methoxy-acid, $N_2R\cdot C_6H_3(OMe)\cdot CO_2H$, was not detected.

Thus benzeneazosalicylic acid [$OH : CO_2H : N_2Ph = 2 : 1 : 5$] yields: (1) *methyl* 5-*benzeneazo*-2-*methoxybenzoate*,

$$N_2Ph\cdot C_6H_3(OMe)\cdot CO_2Me \ [N_2Ph : CO_2H : OMe = 5 : 1 : 2],$$

which separates from alcohol in crystals, m. p. 63—64°; (2) *methyl* 5-*benzeneazosalicylate*, $N_2Ph\cdot C_6H_3(OH)\cdot CO_2Me$, is deposited from alcohol in yellow crystals having a metallic lustre, m. p. 162—165°.

The *p*-chlorobenzeneazo-derivative of *m*-hydroxybenzoic acid gives: (1) *methyl* 6-p-*chlorobenzeneazo*-3-*methoxybenzoate*,

$$C_6H_4Cl\cdot N_2\cdot C_6H_3(OMe)\cdot CO_2Me \ [C_6H_4Cl\cdot N_2 : CO_2Me : OMe = 6 : 1 : 3],$$

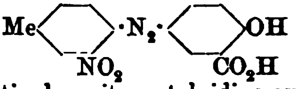
which separates from alcohol in orange-yellow crystals, m. p. 89—90°; (2) *methyl* 6-p-*chlorobenzeneazo*-3-*hydroxybenzoate*,

$$C_6H_4Cl\cdot N_2\cdot C_6H_3(OH)\cdot CO_2Me,$$

which is deposited from alcohol in shining red crystals, m. p. 155°.

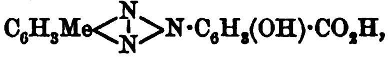
T. H. P.

Reduction of *o*-Nitroazosalicylic Acids by means of Sodium Hyposulphite. EUGÈNE GRANDMOUGIN and J. R. GUISAN (*Ber.*, 1907, 40, 4205—4208. Compare this vol., i, 166).—Further investigation shows that the reduction of *o*-nitroazo-compounds by means of sodium hyposulphite does not always cease when the azoimino-oxide stage is reached, the corresponding triazole compounds being sometimes obtained directly by further action. In other cases, the two compounds are produced together. Both the *o*-nitroazosalicylic acids dealt with in the present paper give triazole derivatives on reduction with sodium hyposulphite.

o-*Nitrotolueneazosalicylic acid*, , prepared either by the interaction of diazotised *m*-nitro-*p*-toluidine and salicylic acid in alkaline solution or by the nitration of *p*-tolueneazosalicylic acid in concentrated sulphuric acid, crystallises from aqueous alcohol in felted masses of long, yellow needles, m. p. 213°. The *acetyl* derivative crystallises from aqueous alcohol in pale yellow needles, m. p. 167°.

p-*Tolueneazosalicylic acid*, $C_{14}H_{12}O_3N_2$, prepared either from the dye "flavazol," which is its sodium salt, or from diazotised *p*-toluidine and salicylic acid, crystallises from aqueous alcohol in brown leaflets, m. p. 212—213°, and yields an *acetyl* compound, $C_{16}H_{14}O_4N_2$, which forms pale yellow crystals, m. p. 157°.

4′-*Hydroxy-2-phenyl-5-methyl*-1 : 2 : 3-*benzotriazole*-3′-*carboxylic acid*,



$$C_6H_3Me<\overset{N}{\underset{N}{|}}>N\cdot C_6H_3(OH)\cdot CO_2H,$$

prepared by reducing *o*-nitrotolueneazosalicylic acid in alkaline solution by means of sodium hyposulphite, crystallises from alcohol or acetic acid in white needles, m. p. 276° (slight decomp.). Its *acetyl* derivative, $C_{16}H_{13}O_4N_3$, crystallises from aqueous alcohol in slender, white needles, m. p. 198°.

The reduction of *o*-nitrobenzeneazosalicylic acid (compare Elbs and Keiper, Abstr., 1903, i, 662) in alkaline solution by means of sodium hyposulphite yields benzotriazole-2-salicylic acid (Elbs and Keiper, *loc. cit.*). T. H. P.

Steric Hindrance. HUGO KAUFFMANN and W. FRANCK (*Ber.*, 1907, 40, 3999—4015. Compare Abstr., 1906, i, 841).—It is suggested in view of the hypothesis of the divisibility of valencies that the steric hindrance observed with ortho-substituted compounds may arise from mutual interference of the partial valencies. The following cases of steric hindrance have been observed with 2-substituted resorcinol dimethyl ethers. 2-Nitroresorcinol dimethyl ether is reduced only with great difficulty by zinc dust in alkaline solution. 2-Aminoresorcinol dimethyl ether cannot be acetylated by the ordinary methods, and does not form a benzylidene derivative; it is diazotised by nitrous acid, and reacts with carbon disulphide, forming a thiocarbamide only extremely slowly. The diazo-sulphate formed from 2-aminoresorcinol dimethyl ether is stable, can be recrystallised from alcohol, remains unchanged on prolonged boiling with water, yields a nitro-derivative when heated with fuming nitric acid, and when boiled with a solution of cuprous cyanide in potassium cyanide forms a stable copper compound which again forms the diazo-salt on treatment with acids. On the other hand, substitution in the nucleus takes place readily; 2-nitroresorcinol dimethyl ether is easily brominated and nitrated, and condenses readily with aldehydes. The steric hindrance observed does not in any case amount to inhibition; its extent depends on the reagent, since 2-aminoresorcinol dimethyl ether reacts only with great difficulty with acetic acid, acetic anhydride, or benzaldehyde, but readily enters into reaction with phenylthiocarbimide or ethyl iodide.

2-Nitroresorcinol dimethyl ether is prepared in an 85% yield by the action of methyl sulphate on 2-nitroresorcinol in 10% aqueous sodium hydroxide solution at 70—80°; it remains almost unchanged when boiled with alcoholic potassium hydroxide. When treated with a limited amount of bromine in glacial acetic acid solution, it forms *bromo-2-nitroresorcinol dimethyl ether*, $C_8H_8O_4NBr$, m. p. 55—56°, or with an excess of bromine the *dibromo*-derivative, $C_8H_7O_4NBr_2$, which crystallises in white needles, m. p. 100—101°.

The action of fuming nitric acid on 2-nitroresorcinol dimethyl ether leads to the formation of two products. 2:4-*Dinitroresorcinol dimethyl ether*, $C_8H_8O_6N_2$, formed at the ordinary temperature, crystallises in yellowish-white needles, m. p. 72°, or after fusion and resolidification, m. p. 62°. 2:4:6-Trinitroresorcinol dimethyl ether, m. p. 124—125°, formed by the boiling acid, is identical with Hönig's styphnic acid dimethyl ether (Abstr., 1878, 727). Whilst the dinitro-ether is only slowly attacked by boiling aqueous sodium hydroxide, the trinitro-ether is rapidly hydrolysed, forming 2:4:6-trinitroresorcinol.

In presence of sulphuric acid, 2-nitroresorcinol dimethyl ether condenses with chloral hydrate, forming 3:3′-*dinitro*-2:4:2′:4′-*tetramethoxydiphenyltrichloroethane*, $CCl_3\cdot CH[C_6H_2(OMe)_2NO_2]_2$, which separates from benzene-light petroleum in yellow crystals, m. p. 181—182°.

2-Nitroresorcinol dimethyl ether is reduced only to a small extent by zinc dust in boiling alcoholic potassium hydroxide or by sodium and amyl alcohol, but readily by iron powder in glacial acetic acid or by tin and hydrochloric acid, forming 2-*aminoresorcinol dimethyl ether*, $C_8H_{11}O_2N$, which crystallises in white leaflets, m. p. 75°, b. p. 146°/23 mm. The *acetyl* derivative, $C_{10}H_{13}O_3N$, is formed by heating the base with acetic anhydride in a sealed tube at 150—160° for ten hours; it crystallises in white leaflets, m. p. 81°, and is hydrolysed by boiling hydrochloric acid. 2:6:2′:6′-*Tetramethoxy-s-diphenylthiocarbamide*, $C_{17}H_{20}O_4N_2S$, m. p. 170°, is formed in only small amount when the amine is boiled with carbon disulphide and alcoholic potassium hydroxide, but in slightly better yields if sulphur is employed in place of potassium hydroxide (compare Hugershoff, Abstr., 1899, i, 886). 2:6-*Dimethoxy-s-diphenylthiocarbamide*, $C_{15}H_{16}O_2N_2S$, m. p. 150°, on the other hand, is formed rapidly with slight development of heat when the amine is shaken with phenolthiocarbimide.

2 : 6-*Dimethoxydiethylaniline*, prepared by boiling 2-aminoresorcinol dimethyl ether with ethyl iodide in a reflux apparatus on the water-bath, is obtained as an almost colourless oil, b. p. 130°/12 mm.; the *platinichloride*, $(C_{12}H_{19}O_2N)_2,H_2PtCl_6$, was analysed. With sodium nitrite in acid solution, the base forms a *dinitro*-derivative, $C_{10}H_{13}O_6N_3$, which is obtained in yellowish-brown crystals, m. p. 108°.

A soluble *diazo-chloride* is obtained when 2-aminoresorcinol dimethyl ether is treated with sodium nitrite and hydrochloric acid at the ordinary temperature and then heated gradually to 60—70°; nitrogen is not evolved when the solution is nearly neutralised with sodium hydroxide and evaporated to dryness. The *diazo-sulphate*,

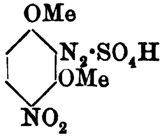
$$C_6H_3(OMe)_2\cdot N_2\cdot HSO_4,$$

prepared by diazotisation with amyl nitrite in alcoholic solution, forms yellow crystals, is stable when free from amyl nitrite, burns quietly on platinum, can be recrystallised from benzoyl chloride, and remains unchanged when boiled with water or hydrochloric acid, or when heated at 300° with concentrated sulphuric acid, but is decomposed by aqueous alkalis, forming resorcinol dimethyl ether. On addition of a concentrated solution of the diazosulphate to 50% aqueous sodium hydroxide, a white *substance* separates, which couples only slowly with alkaline β-naphthol, behaving therefore as an *anti*-diazo-oxide. The diazo-salt couples with β-naphthol in alkaline solution, forming 2 : 6-*dimethoxybenzeneazo-β-naphthol*, $C_6H_3(OMe)_2\cdot N_2\cdot C_{10}H_6\cdot OH$, which crystallises in red needles, m. p. 120—121°, and is not fluorescent. When boiled with fuming nitric acid, the diazo-sulphate yields a *nitro*-derivative having probably the annexed constitution, which couples with alkaline β-naphthol forming a *dye*, $C_{18}H_{15}O_5N_3$, crystallising in red needles, m. p. 162—163°. The *diazo-perbromide*, $C_8H_9O_2N_2Br_3$, prepared by adding potassium bromide and aqueous bromine to the diazo-sulphate, crystallises in needles, decomp. 120°, and loses bromine in contact with water slowly at the ordinary temperature, but quickly on heating. At the ordinary temperature, the perbromide changes slowly into a red *substance*, which couples to only a small extent. A yellowish-brown *salt*, having approximately the composition:

$$C_8H_9O_2N_2,CN,(CuCN)_2,$$

formed by the action of cuprous cyanide in potassium cyanide solution on the diazo-sulphate in presence of sulphuric acid, dissolves in hydrochloric acid, forming a solution which couples with β-naphthol and yields resorcinol dimethyl ether when heated with alkalis. A yellow *substance*, containing tin, formed by the action of stannous chloride and concentrated hydrochloric acid on the diazo-sulphate, behaves in the same manner. 2-*Iodoresorcinol dimethyl ether*, $C_8H_9O_2I$, prepared by heating the diazo-sulphate with concentrated aqueous hydriodic acid, crystallises in white needles, m. p. 103°, and does not react with "active" magnesium.

G. Y.



Methods for the Removal of Proteins from Solution. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1907, 5, 365—367. Compare this vol., i, 667, and following abstract).—The precipitation

of proteins by mastic suspensions is incomplete when more than 1% of protein is present in the solution. As the mastic, however, always removes a large proportion of the protein, even from concentrated solutions, complete precipitation may be achieved by adding mastic two or three times at intervals. In many cases, precipitation by China clay is preferable to that by mastic. G. B.

The Behaviour of Electrolytes in Mastic Precipitation. LEONOR MICHAELIS, LUDWIG PINCUSSOHN, and PETER RONA (*Biochem. Zeitsch.*, 1907, **6**, 1—16. Compare Abstr., 1907, i, 667).—A study of the extent to which electrolytes are carried down from a solution in which mastic flocculation occurs. The problem is of practical importance in connexion with the method of removing proteins, described in the preceding abstract. Acids produce flocculation in very small concentrations, and are not at all carried down by the precipitate. Sodium hydroxide is not an efficient precipitating agent, and is not adsorbed either; baryta is more efficient, and is adsorbed to some extent. Mere traces of colloidal ferric hydroxide precipitate the mastic, and are thereby completely adsorbed. Sodium and ammonium chlorides resemble acids in not being adsorbed at all, but are less efficient precipitants. Other metallic salts are still less efficient, and with those of the heavy metals there is partial adsorption of the base. Dextrose, urea, glycine, and hippuric acid are not carried down at all. Very similar results were obtained with China clay instead of mastic. G. B.

Rotatory Power of Proteins Extracted from Cereal Flours by Aqueous Alcohol. LÉON LINDET and LOUIS AMMANN (*Compt. rend.*, 1907, **145**, 253—255; *Bull. Soc. chim.*, 1907, [iv], 1, 968—974). —By fractional precipitation of wheat gliadin dissolved in 70% alcohol by alcohol or water, two gliadins were obtained, a_D $-81{\cdot}6°$ and $-95{\cdot}0°$. The rotatory power of the mixed gliadins (twenty samples) varied between $-81{\cdot}6°$ and $-92{\cdot}7°$.

Rye and barley yielded a protein, hordein, a_D $-137{\cdot}5°$.

Two of the three maisins (a and β) obtained by Donard and Labbé (Abstr., 1903, i, 215, 782) were separated from maize, a_D $-29{\cdot}6°$ (a) and $-40{\cdot}0°$ (β). N. H. J. M.

The Swelling of Fibrin. MARTIN H. FISCHER and GERTRUDE MOORE (*Amer. J. Physiol.*, 1907, **20**, 330—342).—An attempt to explain the variable affinity of colloids for water on physico-chemical lines. As a physiological outcome, it is found that substances which are most effective in diminishing the amount of swelling of fibrin in hydrochloric acid are those which most retard gastric digestion. The absorption of water by frog's muscles is entirely analogous to the absorption of water by fibrin. W. D. H.

The Products Obtained by Boiling Casein with 25% Sulphuric or Concentrated Hydrochloric Acid. EMIL ABDERHALDEN and CASIMIR FUNK (*Zeitsch. physiol. chem.*, 1907, **53**, 19—30).—The amount of glutamic acid produced by the hydrolysis of casein with 25% sulphuric or concentrated hydrochloric acid is much the same, namely, some 10—11%, if the hydrolysis is continued for a sufficient length of time. Anhydrides of dipeptides are also formed in both cases; the amounts, however, are exceedingly small, under 1%. When sulphuric acid is used, the anhydride consists of a mixture of leucinimide and *l*-phenylalanyl-*d*-alanine anhydride, and probably *l*-leucyl-*d*-valine anhydride. The amounts of anhydrides tend to increase as the time of heating is decreased. When hydrochloric acid is used, leucinimide alone is formed.

Amino-acids do not yield diketopiperazine when heated with concentrated hydrochloric acid. J. J. S.

Hydrolysis of the Sodium Salts of Casein. LUCIUS L. VAN SLYKE and DONALD D. VAN SLYKE (*Amer. Chem. J.*, 1907, **38**, 619—626).—Determinations of the quantity of alkali hydroxide required for the neutralisation of casein give results which vary according to the indicator employed. Laqueur and Sackur (Abstr., 1903, i, 300), in determining the equivalent weight of casein, arbitrarily regarded phenolphthalein as giving correct results.

In the hope of obtaining a method of ascertaining the true neutralisation point, the electrical conductivity of solutions of varying amounts of casein in 100 c.c. of *N*/100 sodium hydroxide has been determined. Usually when an acid is added to a solution of a strong base, the conductivity gradually decreases until the neutral point is reached, and by plotting the conductivities as ordinates and the amounts of acid added as abscissæ, a curve is obtained as a straight line sloping downwards to the neutral point, at which it breaks sharply. The curve for casein, however, like that for phosphoric acid, is concave and does not show any break. The minimum point is near that at which the solution is neutral to phenolphthalein, but cannot be regarded as representing the true point of neutralisation. E. G.

Dissociation of Solutions of the Neutral Caseinates [Caseinogenates] of Sodium and Ammonium. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1907, **11**, 542—552).—Neutral solutions of the sodium and ammonium salts of caseinogen (termed casein by the author) have been prepared by shaking the respective alkalis with excess of caseinogen and filtering, and the electrical conductivity of these salts in various dilutions has been measured at 25°. The variation of the conductivity with dilution is such as to justify the assumption that caseinogen behaves to alkalis as a weak non-amphoteric monobasic acid. From the conductivity results, on the assumption that no complex ions containing sodium are present, the value $2{\cdot}6 \times 10^{-5}$ cm./sec. is obtained for the velocity of the caseinogen ion, but, when the results for the ammonium salt are calculated on the same assumption, it is found that the sum of the velocity of the $NH_4^{\cdot}$ and protein ions is less than the known velocity of the $NH_4^{\cdot}$ ion alone. It follows that the solution of the ammonium salt contains complex ion-protein compounds in which the non-protein ion (in this case $NH_4^{\cdot}$) is not dissociated as such; the formation of such compounds is thus proved for the first time, although their existence had been foreseen by Loeb.

The dissociation constants for the sodium and ammonium salts of caseinogen are 0·0395 and 0·0428 respectively. G. S.

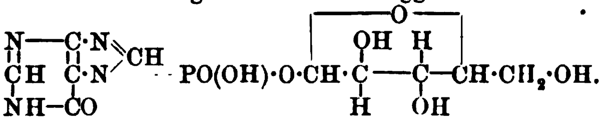
Molecular Weight of Oxyhæmoglobin. Gustav Hüfner and Emil Gansser (*Chem. Zentr.*, 1907, ii, 816; from *Arch. Anat. Physiol. Abt.*, 1907, 209—216).—By means of osmotic pressure measurements, the mol. weight of the hæmoglobin from horses and from oxen was found to be 15,115 and 16,321 respectively, it being still doubtful whether these mol. weights are really different. The authors conclude from their osmotic pressure experiments that crystalline oxyhæmoglobin is composed of one mol. of hæmoglobin combined with one mol. of oxygen. W. H. G.

Paranucleo-protagon. Matthew Steel and William J. Gies (*Amer. J. Physiol.*, 1907, **20**, 378—398).—This is the name given by Ulpiani and Lelli (Abstr., 1902, ii, 573) to a compound in the brain in which they believe the protagon is combined. It is resolved by alcohol into protagon and paranuclein. They further adhere to the idea that protagon is a definite chemical individual. The material is extracted from the brain with chloroform. On the lines of Gies' previous work, the present paper again deals with the non-existence of protagon as a chemical unit, and similarly it is shown that paranucleo-protagon is a mixture also; it contains other substances as well as the two mentioned by Ulpiani and Lelli, and the products differ with the strength and temperature of the alcohol used to decompose it. Probably none of the constituents of protagon are combined with a nuclein-like substance. W. D. H.

Composition of Nucleic Acids of Thymus and Herring-Roe. II. Hermann Steudel (*Zeitsch. physiol. Chem*, 1907, **53**, 14—18. Compare this vol., i, 168).—In addition to guanine, adenine, cytosine and thymine, episaccharic acid (this vol., i, 739) has been isolated from the nucleic acid of thymus by hydrolysis with concentrated nitric acid. The *quinine* salt, $2C_{20}H_{24}O_2N_2,C_6H_{10}O_8$, crystallises well.

It is suggested that the remaining residue in the nucleic acid is $C_{24}H_{44}O_{26}P_4$ and not $C_{21}H_{44}O_{26}P_4$, and the formula for the acid then becomes $C_{48}H_{57}O_{30}N_{15}P_4$. The residue, $C_{24}H_{44}O_{26}P_4$, is supposed on hydrolysis to yield a sugar and metaphosphoric acid. J. J. S.

Inosic Acid. Carl Neuberg and B. Brahn (*Biochem. Zeitsch.*, 1907, **5**, 438—450).—Inosic acid is the only nucleic acid which can at present be obtained pure (as a crystalline salt). Haiser (Abstr., 1895, i, 580) stated that when hydrolysed it is decomposed into phosphoric acid, and probably a purine base and trihydroxyvaleric acid. The second of these products has now been identified as hypoxanthine, and the third as *l*-xylose. Hydrolysis takes place according to the equation: $C_{10}H_{13}O_8N_4P + 2H_2O = H_3PO_4 + C_5H_{10}O_5 + C_5H_4N_4O$. Inosic acid is optically active, $[\alpha]_D$ $-18{\cdot}5^\circ$, a fact which has hitherto been overlooked. The following constitution is suggested:



G. B.

The Constitution of Inosic Acid and the Pentose of Muscle. FRIEDRICH BAUER (*Beitr. chem. Physiol. Path.*, 1907, 10, 345—357).—The author has arrived independently and almost simultaneously at the same general conclusion as Neuberg and Brahn (preceding abstract), namely, that inosic acid is composed of a molecule of phosphoric acid and a molecule of hypoxanthine, which are united by an intermediate pentose molecule in such a way that the latter has lost its free aldehyde group. There is still some disagreement, or doubt, as to the nature of this pentose. The author, who did not observe the optical activity of inosic acid, obtained from it on hydrolysis an osazone, m. p. 158—159°, which he regards as derived from *i*-arabinose, whereas Neuberg and Brahn identify the sugar with *l*-xylose. The dextrorotation, which this latter substance might be expected to produce in the solution after hydrolysis, has, however, not been observed in either investigation.

A full account of the literature and details of a method of preparing crystalline barium inosate is given (yield 3 to 4 grams per kilo. of meat extract used). In meat extract, the sugar of inosic acid occurs in the free state, probably owing to partial hydrolysis during manufacture. G. B.

Tanning and Adsorption Compounds of Gelatin. LÜPPO-CRAMER (*Chem. Zentr.*, 1907, ii, 413—415; from *Zeitsch. Chem. Ind. Kolloide*, 1907, 1, 353—364. Compare Biltz, Abstr., 1904, ii, 324; A. and L. Lumière and Seyewetz, Abstr., 1906, i, 916).—All metallic salts the solutions of which contain a colloidal hydroxide are capable of tanning gelatin. Dilute, but not strong, solutions of ferric salts produce coagulation when added to a solution of gelatin. No coagulation occurs if a ferric salt is added to an ammoniacal solution of gelatin. Ferrous salts, potassium ferrocyanide, and ferricyanide have no tanning action, whereas uranyl salts, auric chloride, and cerium sulphate tan readily. Copper salts and silver nitrate are adsorbed without coagulation. It is impossible to free gelatin treated with a solution of silver bromide in sodium thiosulphate from silver completely by washing; similarly, gelatin treated with mercuric chloride, mercuric iodide, lead iodide, lead nitrate, and barium chloride cannot be freed from these salts by washing.

Gum arabic and albumin behave like gelatin. W. H. G.

Alkaline Digestion. HANS EULER (*Arkiv. Kem. Min. Geol.*, 1907, 2, No. 39, 1—13. Compare this vol., i, 574).—Experiments on the action of pancreatin extract on glycylglycine in presence of small proportions of sodium hydroxide show that the pancreatin combines with a considerable part of the alkali, and, as the effect of the latter on the action is great, extracts of commercial pancreatin and trypsin, unless extremely active, are unsuitable for physico-chemical investigations on dipeptides. The results also show that Schütz-Borissow's rule does not hold for the alkaline digestion of dipeptides.

The pancreatin employed yielded 5·4% of ash, consisting principally of sodium pyrophosphate, probably derived from disodium hydrogen phosphate by heating. The velocity of digestion of glycylglycine by pancreatin in presence of sodium hydroxide is not, however, influenced by the addition of sufficient disodium hydrogen phosphate to double the phosphoric acid present originally. Also, this velocity is not changed by more than 10% of its value by the addition of 0·1 gram of mercuric chloride, 0·12 gram of formaldehyde, or 0·1 gram of potassium cyanide per 100 c.c. of liquid.

The course of the decomposition of glycylglycine by the pressed juice of soaked peas in presence of sodium hydroxide indicates that the excess of the latter is, in this case, far more completely neutralised than by erepsin.

The following results were obtained by the action of 4 grams of very active erepsin on 100 c.c. of 0·1*N*-glycylglycine solution in presence of varying proportions of alkali:

Concentration of alkali	0·035	0·04	0·05	0·06	0·075
Reaction constant, $K \times 1000$...	5·0	7·0	8·3	8·0	6·5

From these results, the conclusion is drawn that alkaline digestive enzymes are not rendered active by the alkali, which accelerates their action partly by neutralising the substrate and partly by preventing the retarding effect of free decomposition products.

The hydrolysis of casein by erepsin is similar to that of glycylglycine. In the former case, however, the destruction of the enzyme is unimportant in comparison with the retardation caused by the decomposition products, whilst with glycylglycine the opposite holds. The reaction coefficient in the case of casein diminishes rapidly as the action proceeds, but the initial velocities are very nearly proportional to the concentrations of the enzyme. Such enzyme solutions, hence, cannot be regarded as heterogeneous systems.

It was further found that the conductivity of faintly alkaline casein solutions gradually diminishes, even in absence of enzyme.

The intensity of the action of erepsin varies for different dipeptides, the values of 1000*K* being 58·4 for alanylglycine, 13·1 for leucylglycine, and 7·0 for glycylglycine.

The decomposition of glycine anhydride by alkali was studied by measuring the conductivity, which was found to diminish considerably as the reaction proceeded, the alkali causing the opening of the ring and the formation of the sodium derivative of glycylglycine. By dilute hydrochloric acid, glycine anhydride is far more slowly decomposed, and here too the velocity rapidly diminishes owing to the combination of the acid with the decomposition products.

Experiments with germinating peas show that, during the ten days from the beginning of germination to the stage at which the lateral roots are developed, the quantity of enzyme capable of decomposing glycylglycine remains practically constant. The enzyme probably exists in the resting seed, either as active enzyme or as proenzyme. This is not the case with the other enzymes of germinating seeds, for instance, with those causing proteolysis. T. H. P.

Action of Arginase on Creatine and other Guanidine Derivatives. Henry D. Dakin (*J. Biol. Chem.*, 1907, 3, 435—441). —Arginase is a specific enzyme for the exclusive hydrolysis of *d*-arginine or of substances containing the *d*-arginine grouping. Creatine and other guanidine derivatives structurally similar to arginine are incapable of hydrolysis by this enzyme. W. D. H.

Specific Accelerating Action of Sodium Fluoride on the Coagulation of Milk by Vegetable Rennet. C. GERBER (*Compt. rend.*, 1907, **145**, 689—692).—The rate of coagulation of milk by vegetable rennet is first slightly accelerated, then retarded by the addition of increasing quantities of sodium fluoride; when the salt is present in the proportion of 30—60 mg. molecules per litre of milk, there is no coagulation, but the process begins again as the proportion of the salt is increased, the rate of coagulation being first accelerated, then retarded. The irregularity of these results is attributed to the disturbing influence introduced by the precipitation of the calcium salts present by the sodium fluoride. If a small quantity of sodium chloride is added to the mixtures, the results are comparable with those previously obtained, and show that the specific action of sodium fluoride is similar to that of sodium chloride. M. A. W.

Systematic Investigation of Oxydases in Animal Tissues. OCTAVE DONY-HÉNAULT and Mlle. J. VAN DUUREN (*Bull. Acad. roy. Belg.*, 1907, 537—638).—In the first part of this memoir, a résumé of current theories explaining catalytic oxidation is given, and the analogies between such actions and those due to oxydases in living tissues are detailed. Attention is then directed to the tests which have been applied by various investigators in ascertaining the occurrence of oxidising ferments in animal organs. Schmiedeberg's test, which consists in estimating the amount of salicylaldehyde converted into salicylic acid by an extract of the organ under investigation, has been fully examined, and it is found that it is liable to three sources of error. In removing the excess of salicylaldehyde as a preliminary to the estimation of the amount of acid formed, a saturated solution of sodium hydrogen sulphite is used, and it is found that this in presence of salicylic acid and ether leads to the formation of some sulphuric acid and organic acids, the latter being apparently produced from the ether. The alkalimetric estimation of the salicylic acid formed gives therefore results which are usually too high. Colorimetric estimation of the salicylic acid by means of ferric chloride only gives trustworthy results when the amount of acid is small and there are no other free acids present. Elion's method (Abstr., 1889, 195), which depends on the conversion of the salicylic acid into tribromophenol, gives good results in the case of pure mixtures of the aldehyde and acid, but it appears to be impossible to extract the whole of the acid by means of ether from albuminous solutions, such as aqueous extracts of organs, so that even using this method the results obtained are low, but a modified form of this method, described in detail in the original, was eventually adopted as the best available.

In the experiments, an extract of calves' livers in salt (0·9%), or sodium fluoride (0·65%) solution, was used. It was found that the oxidation of salicylaldehyde to salicylic acid by such extracts takes place best in the absence of oxygen, and that the velocity of the reaction varies greatly and irregularly when the concentration of the extract varies and is conditioned mainly by the concentration of the aldehyde. The oxidising power of the extracts diminishes spontaneously on keeping, and this diminution in activity usually occurs more rapidly in presence of air, or when the temperature is raised. Some extracts remain active after being heated to 80°, whilst others show a marked lessening of activity after exposure to this temperature. These observations are insufficient to enable a decision to be arrived at as to whether the oxidation is due to an oxydase or is merely catalytic, but the authors are inclined to adopt the latter alternative.

The last portion of the memoir is devoted to a criticism of the views of Abelous and his collaborators (Abstr., 1896, ii, 119; 1898, ii, 36; 1900, i, 268, ii, 226; 1903, ii, 560, 561, 678; 1904, ii, 188) on the subject, and in this connexion it is pointed out that all the extracts used in the present set of experiments contained a small amount of oxyhæmoglobin, which rapidly disappeared when the extracts were exposed to air, but persisted for some time in its absence, which would probably not have been the case if an oxydase had also been present in the solution. Salicylaldehyde is not oxidised by oxyhæmoglobin, so that the latter cannot be the source of the oxygen used in the oxidation of the aldehyde by organic extracts. It is suggested that as oxyhæmoglobin can exist in dilute solution in a vacuum for some days, the current view that the mechanism of oxygen exchange brought about by hæmoglobin is mainly physical is not strictly accurate. T. A. H.

Animal Peroxydases. ERNST VON CZYHLARZ and OTTO VON FÜRTH (*Beitr. chem. Physiol. Path.*, 1907, 10, 358—389).—An attempt to extend to animal oxydases the sharp distinction drawn by Chodat and Bach between (vegetable) direct oxydases and peroxydases, which latter only oxidise in the presence of hydrogen peroxide or of some other peroxide. The guaiacum reaction of blood is due to hæmatin and not to a true peroxydase. The difficulty of completely removing blood from the tissues makes guaiacum tincture an unsuitable reagent for the detection of peroxydases. For tissues containing blood, the liberation in the presence of hydrogen peroxide of iodine from an acidified solution of potassium iodide should be employed.

A spectro-photometric method, based on the oxidation to malachite-green of the leuco-base, has been worked out and employed in the measurement of the velocity of peroxydase action. A graphical representation of the results obtained by this method shows that the oxidation by hæmatin proceeds at a uniform rate, whereas the velocity of that due to animal peroxydase gradually falls off to zero. The peroxide reaction is much more dependent on the concentration of the leuco-base than is the hæmatin reaction.

The oxidation of ammonium sulphide by oxyhæmoglobin is not accelerated by catalase, and there is no ground for the belief that the latter enzyme has a direct oxidative action, as supposed by Ewald (this vol., ii, 184). G. B.

Catalase. Antagonism between Catalases and Peroxydases. Amedeo Herlitzka (*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 473—479).—According to Ewald (this vol., ii, 184), the dissociation of oxyhæmoglobin is a phenomenon connected with the partial pressure of the oxygen of which the relation existing between oxyhæmoglobin and hæmoglobin is a function. This being so, catalase is capable of increasing the velocities of two chemical reactions of different natures, one being independent and the other dependent on the partial pressure of the oxygen, and the one irreversible and the other reversible (compare Herlitzka, this vol., i, 102). Objections are raised to Ewald's results. Further experiments by the author lead to the conclusion that there exists an antagonism between the action of catalase and that of hæmoglobin, or, in general, of the oxydases with respect to the oxidation of guaiacum resin by peroxides, that is, with respect to the formation of active oxygen. Within certain limits, the greater the concentration of the catalase, so much the greater must be the concentration of the peroxydases to produce oxidation. Thus there is direct proof of the protective action exerted by catalase towards the peroxydases destroying and rendering innocuous the peroxides in the organism.
T. H. P.

Thiophenol-5-chlorophosphines and their Derivatives. August Michaelis and G. Linus Linke (*Ber.*, 1907, **40**, 3419—3425. Compare Michaelis, Abstr., 1903, i, 379; Autenrieth and Hildebrand, *ibid.*, 1898, i, 419, 476).—*Thiophenylchlorophosphine*, $SPh\cdot PCl_2$, obtained by heating thiophenol and phosphorus trichloride in a flask fused to a reflux condenser, forms a somewhat thick, colourless liquid, b. p. 125°/10 mm., D^{15} 1·2560. It fumes in contact with the air and has a disagreeable odour. When left exposed to the air for twenty-four hours, hydrogen chloride is evolved and a crystalline mass consisting of triphenyl trithiophosphite, $P(SPh)_3$, and phosphorous acid is obtained; but when the chlorophosphine is poured into water, a violent reaction occurs, and the products are hydrochloric and phosphorous acids and thiophenol. A thiophosphorous acid has not been obtained. With alcohol, the products are hydrogen chloride, thiophenol, and triethyl phosphite, and with sodium ethoxide, triethyl trithiophosphite, triethyl phosphite, and sodium chloride. The thiolphenylchlorophosphine reacts with chlorine yielding phenyl disulphide and phosphorus trichloride. Thiophenol and phosphoryl chloride yield phosphorus trichloride, phenyl disulphide, and phosphoric acid.

Thiolphenylthionchlorophosphine, $SPh\cdot PSCl_2$, obtained by heating the the thiolphenylchlorophosphine with sulphur at 120° for five hours and distilling the product under reduced pressure, forms a thick, colourless liquid with an aromatic odour, b. p. 168—170°/16 mm., and is not appreciably acted on by water.

A quantitative yield of *triphenyl trithiophosphite*, $P(SPh)_3$, is obtained when phosphorus trichloride is heated with three equivalents of thiophenol at 150° in an oil-bath. It crystallises from ether in short, monoclinic prisms or from alcohol in pointed crystals, m. p. 76—77°. With concentrated sulphuric acid, it yields thiophenol and phosphorus acid, and the same products are formed when the trithiophenyl derivative is heated with water or alcohol under pressure. Triphenyl trithiophosphite readily combines with oxygen, sulphur, or selenium, but is decomposed by chlorine yielding phenyl disulphide and phosphorus trichloride.

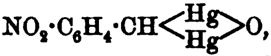
Trithiolphenylphosphine oxide, $O\colon P(SPh)_3$, obtained by the action of hydrogen peroxide on the phosphine, crystallises from ether in strongly refracting, monoclinic prisms, m. p. 115°. It may also be prepared by the action of phosphorus oxychloride on sodium thiophenol, but the product described by Schwarze (*J. pr. Chem.*, 1874, [ii], 10, 234) was probably phenyl disulphide.

Trithiolphenylphosphine sulphide, $S\colon P(SPh)_3$, crystallises from alcohol in plates, m. p. 86°. It is obtained by the direct addition of sulphur in carbon disulphide solution at 120°, or by the action of phosphorus sulphochloride on sodium thiophenol.

Trithiolphenylphosphine selenide, $Se\colon P(SPh)_3$, crystallises from ether in pale yellow, monoclinic plates, m. p. 95°. Secondary chlorophosphines have not been prepared. J. J. S.

Mercury Compounds from Nitrotoluenes. ARNOLD REISSERT (*Ber.*, 1907, **40**, 4209—4226. Compare this vol., i, 908).—Although aromatic amines and phenols readily admit of the entry of mercury atoms into their molecules, nitrobenzene has but slight tendency to react in this way. The author finds, however, that *o*- and *p*-nitrotoluenes are readily converted into mercury derivatives when boiled with mercuric oxide in presence of sodium hydroxide, the mercury in these cases entering the side-chain. The compounds yielded by *p*-nitrotoluene and 2 : 4-dinitrotoluene have not been obtained in a pure state, but from *o*-nitrotoluene two well-characterised chemical individuals have been prepared.

o-Nitromercuribenzyl chloride, $NO_2\cdot C_6H_4\cdot CH_2\cdot HgCl$, obtained by boiling dilute sodium hydroxide solution containing *o*-nitrotoluene in suspension with precipitated mercuric oxide, is precipitated from ammoniacal solution by hydrochloric acid in bundles of colourless needles, m. p. 145—146°.

o-*Nitrodimercuribenzylidene oxide*,  $NO_2\cdot C_6H_4\cdot CH{<}{\substack{Hg\\Hg}}{>}O$, obtained by protracted boiling of sodium hydroxide solution, *o*-nitrotoluene, and mercuric oxide, is precipitated from acetic acid solution by excess of sodium hydroxide in dark yellow, crystalline masses decomposing at above 220°. The following salts were prepared: the ***sulphate***,

$$NO_2\cdot C_6H_4\cdot CH\colon Hg_2\colon SO_4,$$

crystallising in pale yellow, broad needles or plates; ***basic sulphate***, $[NO_2\cdot C_6H_4\cdot CH(Hg\cdot OH)Hg]_2SO_4$, forming a heavy, orange-yellow powder; ***chloride***, $NO_2\cdot C_6H_4\cdot CH(HgCl)_2$, a pale yellow, amorphous compound; ***hydroxychloride***, $NO_2\cdot C_6H_4\cdot CH(HgCl)\cdot Hg\cdot OH$; ***nitrate***, and ***nitrite***, $NO_2\cdot C_6H_4\cdot CH(Hg\cdot NO_2)_2$.

o-Nitrodimercuribenzylidene oxide is partially decomposed by dydrogen sulphide into mercuric sulphide and *o*-nitrotoluene. By zinc hust and sulphuric acid, it is reduced to *o*-toluidine and mercury. When heated with nitrous acid, it gives *o*-nitrobenzaldehyde, which is also formed together with a small proportion of *o*-dinitrotolane,

$$NO_2\cdot C_6H_4\cdot C{\vdots}C\cdot C_6H_4\cdot NO_2\ (?),$$

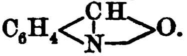
by boiling it with nitric acid. When treated in the cold with nitrous and hydrochloric acids, it is converted into approximately molecular proportions of *o*-nitrobenzaldehyde and its oxime; the dinitrite formed by the nitrous acid is converted by hydrochloric acid into the oxime by way of a hypothetical nitroso-derivative:

$$NO_2\cdot C_6H_4\cdot CH(HgNO_2)_2 + 2HCl = HNO_2 + H_2O + NO_2\cdot C_6H_4\cdot C(NO)(HgCl)_2,$$

and the latter: $+ 2HCl = NO_2\cdot C_6H_4\cdot CH{:}NOH + 2HgCl_2$, one half of the oxime formed being then transformed into the aldehyde as follows:

$$2NO_2\cdot C_6H_4\cdot CH{:}NOH + 4HNO_2 = 2NO_2\cdot C_6H_4\cdot CHO + 4NO + N_2O + 3H_2O.$$

Towards acids and alkalis, *o*-nitrodimercuribenzylidene oxide is, in general, very stable, but, when boiled with 20% hydrochloric acid solution, it is transformed into anthranil,



$C_6H_4{<}\begin{matrix}CH\\ |\\ N\end{matrix}{>}O$.

The action of chlorine, best in presence of excess of hydrochloric acid, on *o*-nitrodimercuribenzylidene oxide yields o-***nitrobenzylidene chloride***, $NO_2\cdot C_6H_4\cdot CHCl_2$, which, in a slightly impure condition, is a faintly red oil, b. p. 150—151°/10 mm. Similarly, the action of bromine yields the corresponding bromide and that of iodine, o-***nitrobenzylidene iodide***, $NO_2\cdot C_6H_4\cdot CHI_2$, which crystallises from alcohol in yellow prisms, m. p. 70—72°.

The interaction of *p*-nitrotoluene and precipitated mercuric oxide in presence of sodium hydroxide yields p-***nitrodimercuribenzylidene oxide***, which was not obtained pure and which is converted into *p*-nitrobenzoic acid by the action of dilute nitric acid.

Similarly, 2 : 4-dinitrotoluene is converted almost quantitatively into 2 : 4-***dinitrodimercuribenzylidene oxide***, which is converted into mercuric sulphide and 2 : 4-dinitrotoluene by hydrogen sulphide, into 2 : 4-dinitrotoluene by 10% hydrochloric acid, and into 2 : 4-dinitrobenzoic acid by concentrated nitric acid. T. H. P.

JOURNAL
OF
THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS
ON
PHYSICAL, INORGANIC, MINERALOGICAL, PHYSIOLOGICAL, AGRICULTURAL, AND ANALYTICAL CHEMISTRY.

Committee of Publication:

H. E. Armstrong, Ph.D., LL.D., F.R.S.
E. C. C. Baly.
Horace T. Brown, LL.D., F.R.S.
A. W. Crossley, D.Sc., Ph.D., F.R.S.
Wyndham R. Dunstan, D.Sc., Ph.D., F.R.S.
M. O. Forster, D.Sc., Ph.D., F.R.S.
R. Meldola, F.R.S.
G. T. Morgan, D.Sc.
Sir W. Ramsay, K.C.B., LL.D., F.R.S.
A. Scott, M.A., D.Sc., F.R.S.
W. A. Tilden, D.Sc., F.R.S.
John Wade, D.Sc.

Editor:
J. C. Cain, D.Sc., Ph.D.

Sub-Editor:
A. J. Greenaway.

Assistant Sub-Editor:
C. H. Desch, D.Sc., Ph.D.

Abstractors:

E. F. Armstrong, Ph.D., D.Sc.
C. F. Baker, Ph.D., B.Sc.
G. Barger, M.A., D.Sc.
W. A. Davis, B.Sc.
H. M. Dawson, Ph.D., B.Sc.
T. Ewan, B.Sc., Ph.D.
W. H. Glover, Ph.D.
E. Goulding, B.Sc.
P. Haas, B.Sc., Ph.D.
W. D. Halliburton, M.D., F.R.S.
T. A. Henry, D.Sc.
E. Horton, B.Sc.
L. M. Jones, B.Sc.
Z. Kahan, B.Sc.
L. De Koningh.
A. McKenzie, M.A., D.Sc.
N. H. J. Miller, Ph.D.
G. T. Morgan, D.Sc.
K. J. P. Orton, M.A., Ph.D.
J. C. Philip, M.A., Ph.D.
T. H. Pope, B.Sc.
W. Robertson.
G. Senter, Ph.D., B.Sc.
W. P. Skertchly.
C. Smith, D.Sc.
L. J. Spencer, M.A.
J. J. Sudborough, Ph.D., D.Sc.
A. Jamieson Walker, Ph.D., B.A.
E. W. Wheelwright, B.A., Ph.D.
M. A. Whiteley, D.Sc.
G. Young, Ph.D.

1907. Vol. XCII. Part II.

LONDON:
GURNEY & JACKSON, 10, PATERNOSTER ROW.
1907.

RICHARD CLAY & SONS, LIMITED,
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

I.—Pinene Nitrolamine. By **Frederick Peacock Leach** . 1

II.—A *pseudo*-Semicarbazide from Pinene. By **Frederick Peacock Leach** 10

III.—The Liquid Volume of a Dissolved Substance. By **John Scott Lumsden** 24

IV.—The Influence of Light on Diazo-reactions. I. By **Kennedy Joseph Previté Orton**, **Joseph Edward Coates** (and, in part, **Frances Burdett**) 35

V.—On the More Exact Determination of the Densities of Crystals. By The **Earl of Berkeley** 56

VI.—Action of Reducing Agents on 5-Chloro-3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene. By **Arthur William Crossley** and **Nora Renouf**, Salters' Research Fellow . 63

VII.—The Viscosity of Liquid Mixtures. By **Albert Ernest Dunstan** and **Robert William Wilson** 83

VIII.—Relation between Chemical Constitution and Physiological Action in the Tropeines. By **Hooper Albert Dickinson Jowett** and **Frank Lee Pyman** 92

IX.—4-Hydroxyphthalic and 4-Methoxyphthalic Acids. By **William Henry Bentley** and **Charles Weizmann** . . 98

X.—3-Hydroxyphthalic and 3-Methoxyphthalic Acids and their Derivatives. By **William Henry Bentley**, **Rona Robinson**, and **Charles Weizmann** 104

XI.—A Relation between the Volumes of the Atoms of Certain Organic Compounds at the Melting Point and their Valencies. Interpretation by Means of the Barlow-Pope Theory. By **Gervaise Le Bas**, B.Sc. 112

XII.—The Optical Influence of Contiguity of Unsaturated Groups. By **Julius Wilhelm Brühl** 115

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E., and A. Schittenhelm, i, 104.
Abderhalden, E., and Y. Teruuchi, i, 104.
Achelis, W., ii, 41.
Adam, R. See R. Möhlau.
Aggazzotti, A., ii, 37.
Alber, E. See F. Fichter.
Alcock, F. H., ii, 58.
Alden, F. W., ii, 54.
Ambardanoff. See C. A. Bischoff.
Arbasoff, A. E., i, 8.
Armstrong, H. E., ii, 13.
Armstrong, H. E., and E. Ormerod, i, 103.
Arnaud, A. See H. Pellet.
Arnost, A., ii, 59.
Arntz, K. See O. Fischer.
Auer, J. See S. J. Meltzer.
Autenrieth, W., and P. Mühlinghaus, i, 31.

B.

Bamberger, M., and A. Landsiedl, ii, 45.
Barger, G., and H. H. Dale, i, 79.
Barnes, S. K. See C. L. Parsons.
Bartell, K. See F. W. Semmler.
Baubigny, H., ii, 21.
Baumgarten, A., and E. P. Pick, ii, 42.
Baumgarten, A., and H. Popper, ii, 41.
Baur, E., and E. Polenske, ii, 56.
Baxter, G. P., and M. A. Hines, ii, 28.
Beccard, E. See O. Diels.
Beck, K., and K. Ebbinghaus, ii, 8.
Beckenkamp, J., ii, 34.
Beckmann, E., and W. Gabel, ii, 24.
Bellucci, I., and C. Cecchetti, ii, 29.
Benedicks, C., ii, 36.
Benedict, S. R., ii, 52.
Bentley, W. H., R. Robinson, and C. Weizmann, TRANS., 104.
Bentley, W. H., and C. Weizmann, TRANS., 98.
Berkeley, The Earl of, TRANS., 56.
Berthelot, M., i, 9.
Bertrand, G., i, 68.
Bertrand, G., and M. Javillier, ii, 53.
Beschke, E. See J. von Braun.
Bickel, A., ii, 38.
Bieber, A. See A. Kötz.
Bigelow, W. D., and F. C. Cook, ii, 60.
Bigler, P., and S. von Kostanecki, i, 76.
Bihmann, J. See C. A. Bischoff.
Binet du Jassoneix, A., ii, 30.
Biquard, R. See C. Moureu.
Bischoff, C. A., A. Blumenthal, K. Kowerski, i, 84.
Bischoff, C. A., and E. Fröhlich, i, 28.
Bischoff, C. A., M. Gussew, J. Wielowieyski, and A. Willums, i, 34.
Bischoff, C. A., Ambardanoff, and Schmähling, i, 35.
Bischoff, C. A., J. Bihmann, A. Gussew, K. Smolnikoff, and W. Wachsmuth, i, 32.
Blumenthal, A. See C. A. Bischoff.
Boedecker, F. See O. Wallach.
Bödtker, E., i, 27.
Boehringer, R. See F. Fichter.
Böhm, R., i, 15.
Bornwater, J. T. See F. A. H. Schreinemakers.
Borsche, W., and A. Fels, i, 80.
Borsche, W., and A. Heyde, i, 31.
Brand, K., and E. Stohr, i, 100.
Braun, B., and H. Kittel, i, 16.

Braun, J. von, and E. Beschke, i, 79.
Braun, J. von, and C. Müller, i, 28.
Briner, E., ii, 11.
Brögger, W. C., ii, 36.
Brown, O. W., ii, 31.
Brühl, J. W., TRANS., 115.
Brun, A., ii, 33.
Buchner, E., J. Meisenheimer, and H. Schade, i, 17.
Bülow, C., i, 99.
Burdett, F. See K. J. P. Orton.
Burger, A., ii, 30.
Burgess, C. F., and S. G. Engle, ii, 29.
Butler, T. H., i, 54.

C.

Caldwell, R. J., ii, 14.
Campbell, F. H., ii, 24.
Cantoni, H., and M. Rosenstein, ii, 54.
Carl, H. See E. Fischer.
Caron, and Raquet, ii, 52.
Carson, C. M. See A. Smith.
Catel, J. See A. Guyot.
Cecchetti, C. See I. Bellucci.
Chablay, E., i, 53.
Chabrié, C., and F. Levallois, ii, 35.
Chamberlain, J. S., ii, 46.
Chieffi, G. See C. Ulpiani.
Ciamician, G., and P. Silber, i, 19.
Ciusa, R., i, 62.
Ciusa, R. See also G. Plancher.
Clark, F. E. See C. McCheyne Gordon.
Coates, J. E. See K. J. P. Orton.
Coffignier, C., i, 67.
Cook, F. C. See W. D. Bigelow.
Courant, S., and S. von Kostanecki, i, 75.
Crépieux, P. See F. Reverdin.
Crossley, A. W., and N. Renouf, TRANS., 63.
Cuisinier, L. See F. Reverdin.
Curtius, T., A. Darapsky, and E. Müller, i, 21.
Curtius, T., and J. Thompson, i, 95.

D.

Daalen, C. K. van, ii, 58.
Dale, H. H. See G. Barger.
Darapsky, A. See T. Curtius.
Dax, R., ii, 37.
Deckers, A., ii, 53.
Delacre, M., i, 7.
Delaite, J., and J. Legrand, ii, 57.
Deprat, J., ii, 36.
Diels, O., and E. Beccard, i, 56.
Dijk, G. van, ii, 8.
Dimroth, O., i, 21.
Dimroth, O., and M. Eble, i, 57.
Dimroth, O., E. Frisoni, and J. Marshall, i, 97.
Dimroth, O., and L. Taub, i, 96.
Dorp, jun., W. A. van. See F. A. H. Schreinemakers.
Dubois, W. L., ii, 58.
Dufour, A., ii, 1.
Dunger, R., ii, 41.
Dunstan, A. E., and R. W. Wilson, TRANS., 83.

E.

Ebbinghaus, K. See K. Beck.
Eble, M. See O. Dimroth.
Ehrlich, F., ii, 44.
Engle, S. G. See C. F. Burgess.

F.

Fabinyi, R., and T. Széki, i, 45.
Falckenstein, V. von, ii, 19.
Falk, K. G., ii, 18.
Fels, A. See W. Borsche.
Fichter, F., and R. Boehringer, i, 92.
Fichter, F., E. Alber, G. Füeg, W. Latzko, K. Philipp, E. Preiswerk, G. Rosenberger, E. Tschudin, and R. Vortisch, i, 81.
Fiederer, M. See R. F. Weinland.
Fiorentino, G. See L. Marino.
Fischer, E., i, 25.
Fischer, E., and H. Carl, i, 9.
Fischer, E., and K. Raske, i, 18.
Fischer, O., and K. Arntz, i, 94.
Fitschy, P., ii, 45.
Fleischmann, F. See F. Haber.
Foerster, F., ii, 54.
Fokin, S., i, 10.
Formánek, J., i, 88.
Francis, F. E., i, 53.
Franke, H., ii, 60.
Freundler, P., i, 13.
Friedheim, C., ii, 53.
Frisoni, E. See O. Dimroth.
Fröhlich, E. See C. A. Bischoff.
Fröhlich, F. W., ii, 40.
Froehner, A., ii, 58.
Fuchs, K., ii, 17.
Füeg, G. See F. Fichter.
Fürth, A., i, 61.
Funke, P., & Co., ii, 18.

G.

Gabel, W. See E. Beckmann.
Gabriel, S., i, 90.
Gain, G., ii, 32.
Gaubert, P., ii, 24.
Gauthier, D., i, 20.
Gawalowski, A., ii, 21, 25, 27.
Gelmo, P., i, 31.
Glaessner, K., and E. P. Pick, ii, 41.
Gleditsch, Mlle. E., i, 24.
Glover, W. H. See A. Hantzsch.
Goettsch, H. M., ii, 4.
Goettsch, H. M. See also H. N. McCoy.
Goldschmiedt, G., i, 30.
Gordin, H. M., i, 68.
Gordon, C. McCheyne, and F. E. Clark, ii, 5.
Gossner, B., ii, 16.
Grafe, V., and K. Linsbauer, ii, 45.
Grandmougin, E., i, 101.
Gréhant, N., ii, 49.
Guichard, M., ii, 32.
Guleke, N., ii, 42.
Gussew, A. See C. A. Bischoff.
Gussew, M. See C. A. Bischoff.
Gutbier, A., and M. Woernle, i, 87.
Guthrie, C. C., F. H. Pike, and G. N. Stewart, ii, 40.
Gutzeit, E., ii, 50.
Guyot, A., and J. Catel, i, 76.

H.

Haber, F., and F. Fleischmann, ii, 6.
Haensel, H., i, 65.
Haller, A., i, 9.
Haller, A., and Youssoufian, i, 10.
Hamburger, H. J., ii, 13.
Hansen, C. See V. Henriques.
Hantzsch, A., and W. H. Glover, i, 101.
Harden, A., and W. J. Young, i, 104.
Hari, P. See F. Tangl.
Harries, C. D., i, 11.
Harries, C. D., and H. O. Türk, i, 11.
Harzer, A. See A. Kötz.
Hassreidter, V., ii, 50.
Headden, W. P., ii, 34.
Hébert, A., ii, 43.
Henriques, V., and C. Hansen, ii, 39.
Henry, L., i, 4, 7.
Herbig, W., ii, 59.
Herlitzka, A., i, 102.
Herrmann, F., i, 52.
Herz, W., and B. Mylius, i, 55.
Herzig, J., E. Hornstein, and F. Wenzel, i, 43.
Heyde, A. See W. Borsche.
Hines, M. A. See G. P. Baxter.
Hoffmann, G., ii, 4.
Hoffmann, I. F., ii, 18.
Hoffmann, W., ii, 54.
Hornstein, E. See J. Herzig.
Hürt, H. See H. von Liebig.

I.

Ipatieff, W. N., i, 5, 6.

J.

Jacoby, M., ii, 38.
Javillier, M. See G. Bertrand.
Jessen, H., i, 60, 61.
Jolles, A., ii, 56.
Jorissen, W. P., ii, 48.
Jovitschitsch, M. Z., i, 98.
Jowett, H. A. D., and F. L. Pyman, TRANS., 92.

K.

Kampen, G. B. van, ii, 50.
Kaufmann, H., ii, 3.
Kayser, G. See A. Kötz.
Keller, C., ii, 2.
Kempf, R., i, 63.
Kittel, H. See B. Braun.
Knapp, B., ii, 39.
König, B., and S. von Kostanecki, i, 62.
Kötz, A., A. Bieber, A. Harzer, G Kayser, and P. Schüler, i, 59.
Kötz, A., and A. Michels, i, 58.
Kötz, A., and P. Schüler, i, 58.
Kohlschütter, V., ii, 7.
Kondakoff, I., i, 24.
Konowaloff, M. I., i, 1.
Kostanecki, S. von. See P. Bigler, S. Courant, and B. König.
Kostanecki, S. von, and V. Lampe, i, 73.
Kostanecki, S. von, and J. Tambor, i, 75.
Kowerski, K. See C. A. Bischoff.
Kremann, R., i, 8.
Kučera, B., and B. Mašek, ii, 4
Kutscher, F., i, 18.

L.

Laar, J. J. van, ii, 16.
Lacroix, A., ii, 33.
Lacroix, H , i, 78.
Lampe, V. See S. von Kostanecki.
Landsiedl, A. See M. Bamberger.
Latzko, W. See F. Fichter.
Lavaux, J., i, 25.
Lawrie, J. W., i, 3.
Leach, F. P., Trans., 1, 10.
Le Bas, G., Trans., 112.
Lebedeff, A. F. See A. J. Nabokich.
Le Blanc, M., and K. Novotný, ii, 22.
Legrand, J. See J. Delaite.
Lemoult, P., ii, 10.
Lengyel, R. von. See F. Tangl.
Levallois, F. See C. Chabrié.
Levi, M. G. See R. Nasini.
Lewkowitsch, J., i, 10.
Liebig, H. von, and H. Hürt, i, 45.
Lienau, D., and A. Stutzer, ii, 47.
Linsbauer, K. See V. Grafe.
Lippmann, E. O. von, ii, 45.
Loeb, J., ii, 38.
Longinescu, G. G., ii, 15.
Lotz, W. See H. Rupe.
Ludwinowsky, S., and J. Tambor, i, 75.
Lumsden, J. S., Trans., 24.
Lunge, G., ii, 50.
Lunge, G., and A. Rittener, ii, 51.

M.

McCoy, H. N., and H. M. Goettsch, ii, 5.
Mache, H., and T. Rimmer, ii, 3.
Magnus, R., ii, 42.
Margosches, B. M., ii, 23.
Marino, L., and G. Fiorentino, i, 103.
Marshall, J. See O. Dimroth.
Mascarelli, L., i, 25.
Mašek, B. See B. Kučera.
Mays, K, ii, 38.
Mazzucchelli, A., ii, 54.
Mech, H., i, 63.
Meisenheimer, J. See E. Buchner.
Meltzer, S. J., and J. Auer, ii, 42.
Menschutkin, B. N., i, 19.
Meyer, J., ii, 15.
Mezger, R. See J. Schmidt.
Michels, A. See A. Kötz.
Mieg, W. See R. Willstätter.
Möhlau, R., and R. Adam, i, 40,
Moss, R. J., ii, 20.
Moureu, C., and R. Biquard, ii, 22.
Mühlhausen, G., i, 25.
Mühlinghaus, P. See W. Autenrieth.
Müller, C. See J. von Braun.
Müller, E, ii, 2.
Müller, E. See also T. Curtius.
Müller, H. A., i, 89.
Mylius, B. See W. Herz.

N.

Nabokich, A. J., and A. F. Lebedeff, ii, 43.
Nasini, R., and M. G. Levi, ii, 3.
Neustädter, V., i, 14.
Noda, T., ii, 3.
Novotný, K. See M. Le Blanc.

O.

Oechsner de Coninck, W., ii, 21.
Oddo, G., ii, 15.
Oppermann, H. See T. Posner.
Ormerod, E. See H. E. Armstrong.
Orton, K. J. P., F. Burdett, and J. E. Coates, Trans., 35.

P.

Panchaud, L. See F. Ullmann.
Parrain, i, 43.
Parrozzani, A. See C. Ulpiani.
Parsons, C. L., and S. K. Barnes, ii, 52.
Passerini, N., ii, 44.
Paul, L., i, 43.
Pellet, H., and A. Arnaud, ii, 51.
Perdrix, L., i, 13.
Perotti, R., ii, 48.
Pescheck, E., ii, 50.
Philipp, K. See F. Fichter.
Pick, E. P. See A. Baumgarten, and K. Glaessner.
Piettre, M., and A. Vila, ii, 37.
Pike, F. H. See C. C. Guthrie.
Pinner, A., i, 92.
Plancher, G., and R. Ciusa, i, 80.
Pockels, F., ii, 16.
Polenske, E. See E. Baur.
Popper, H. See A. Baumgarten.
Porcher, C., ii, 56.
Posner, T., and H. Oppermann, i, 55.
Poulsson, E., ii, 39.
Precht, J., ii, 3.
Preiswerk, E. See F. Fichter
Preschor, J., ii, 55.
Pringsheim, H., ii, 44.

Purvis, J. E., ii, 1, 2.
Pyman, F. L. See H. A. D. Jowett.

Q.

Quensel, P. D., ii, 34.

R.

Rabe, P., and K. Ritter, i, 78.
Radcliffe, L. G., ii, 59.
Raquet. See Caron.
Raske, K. See E. Fischer.
Reformatsky, S. See J. Zeltner.
Renouf, N. See A. W. Crossley.
Reverdin, F., and P. Crépieux, i, 42.
Reverdin, F., and L. Cuisinier, i, 37.
Reychler, A., i, 23.
Richardson, O. W., ii, 6.
Riesser, O., i, 77.
Rimmer, T. See H. Mache.
Rinck, A. See B. Wagner.
Ringer, W. E., ii, 55.
Rising, A., i, 42.
Rittener, A. See G. Lunge.
Ritter, K. See P. Rabe.
Robinson, R. See W. H. Bentley.
Rogozinski, F., ii, 40.
Rohland, P., ii, 27.
Romijn, G., ii, 49.
Rosenberger, F., ii, 41.
Rosenberger, G. See F. Fichter.
Rosenstein, M. See H. Cantoni.
Rosenthaler, L., and F. Türk, ii, 12.
Ruer, R., ii, 32.
Ruhland, W., ii, 43.
Rupe, H., and W. Lotz, i, 12, 13.

S.

Salant, W., ii, 40.
Salkind, J., i, 22.
Salvendi, H., ii, 37.
Schade, H. See E. Buchner.
Schall, R. See J. Schmidt.
Schimmel & Co., i, 66.
Schittenhelm, A. See E. Abderhalden.
Schjerning, H., ii, 46.
Schmähling. See C. A. Bischoff.
Schmidlin, J., i, 26, 27, 93.
Schmidt, H. W. ii, 4.
Schmidt, J., and R. Mezger, i, 43.
Schmidt, J., and R. Schall, i, 26.
Scholtz, M., i, 79.
Schreinemakers, F. A. H., ii, 17.
Schreinemakers, F. A. H., and J. T. Bornwater, ii, 23.
Schreinemakers, F. A. H., and W. A. van Dorp, jun., ii, 23.
Schüler, P. See A. Kötz.
Schultze, F. See B. Wagner.
Schumm, O., ii, 40.
Scriba, F., ii, 50.
Semmler, F. W., and K. Bartell i, 11.
Shaffer, P., ii, 38.
Shall, C., ii, 11.
Silber, P. See G. Ciamician.
Smith, A., and C. M. Carson, ii, 20.
Smith, R. H. See J. Zeleny.
Smolnikoff, K. See C. A. Bischoff.
Snyder, C. D., ii, 40.
Somermeier, E. E., ii, 51.
Sommelet, M., i, 21.
Sponagel, P. See F. Ullmann.
Stansbie, J. H., ii, 25.
Stepanoff, A., ii, 50.
Stewart, G. N. See C. C. Guthrie.
Stohr, E. See K. Brand.
Stroman, A., ii, 8.
Stutzer, A., ii, 47, 48.
Stutzer, A. See also D. Lienau.
Suhl, R. See T. Zincke.
Svedberg, T., ii, 17.
Swarts, F., ii, 9.
Széki, T. See R. Fabinyi.
Szydlowski, L., i, 18.

T.

Tambor, J. See S. von Kostanecki, and S. Ludwinowsky.
Tangl, F., P. Hari, and R. von Lengyel, i, 102.
Taub, L. See O. Dimroth.
Taylor, W. W., ii, 18.
Terauchi, Y. See E. Abderhalden.
Thompson, J. See T. Curtius.
Tiffeneau, M., i, 39.
Tolman, L. M., and T. C. Trescot, ii, 57.
Travers, M. W., and F. L. Usher, ii, 8.
Trescot, T. C. See L. M. Tolman.
Tschitschibabin, A. E., i, 8, 27.
Tschudin, E. See F. Fichter.
Tschugaeff, L. A., i, 17.
Türk, F. See L. Rosenthaler.
Türk, H. O. See C. D. Harries.

U.

Ullmann, F., and P. Sponagel, i, 38.

Ullmann, F., and L. Panchaud, i, 63.
Ulpiani, C., and G. Chieffi, i, 54.
Ulpiani, C., and A. Parrozzani, ii, 57.
Urbain, G., ii, 3.
Usher, F. L. See M. W. Travers.
Utermann, A. See O. N. Witt.

V.

Vanzetti, L., i, 18.
Verneuil, A. See G. N. Wyrouboff.
Vignon, L., i, 102.
Vila, A. See M. Piettre.
Vogelsang, W. See W. Windisch.
Vortisch, R. See F. Fichter.

W.

Wachsmuth, W. See C. A. Bischoff.
Wagner, B., A. Rinck, and F. Schultze, ii, 49.
Wallach, O., and F. Boedecker, i, 64.
Walter, B., ii, 2.
Watts, O. P., ii, 31.
Wegscheider, R., i, 60.
Wehmer, C., ii, 44.
Wein, E., ii, 48.
Weinland, R. F., and M. Fiederer, ii, 31.
Weizmann, C. See W. H. Bentley.
Welsbach, C. A. von, ii, 26.
Wenzel, F. See J. Herzig.
Wielowieyski, J. See C. A. Bischoff.
Willanen, K., ii, 39.
Willums, A. See C. A. Bischoff.
Willstätter, R., i, 71.
Willstätter, R., and W. Mieg, i, 69.
Wilson, R. W. See A. E. Dunstan.
Windaus, A., i, 90.
Windisch, W., and W. Vogelsang, ii, 46.
Winkelblech, K., ii, 17.
Witt, O. N., and A. Utermann, i, 27.
Wöhler, L., ii, 33.
Woernle, M. See A. Gutbier.
Wohlgemuth, J., ii, 43.
Wollenweber, W., i, 72.
Wyrouboff, G. N., and A. Verneuil, ii, 26.

Y.

Yégounow, M., ii, 12.
Young, S., ii, 9.
Young, W. J. See A. Harden.
Youssoufian. See A. Haller.

Z.

Zeleny, J., and R. H. Smith, ii, 21.
Zeltner, J., and S. Reformatsky, i, 23.
Zincke, T., and R. Suhl, i, 37.

ABBREVIATIONS IN ABSTRACTS.

The following abbreviated forms will be used in the abstracts in place of the expressions in use previously:

Old form.	New form.
Melts at *or* melting at	m. p.
Boils at *or* boiling at 240° under 35 mm. pressure	b. p. 240°/35 mm.
Sp. gr. 1·462 at 20°/4°	D_4^{20} 1·462.
$\alpha_D + 3{\cdot}48°$ at 17°	$\alpha_D^{17} + 3{\cdot}48°$.
$[\alpha]_D + 26{\cdot}5°$ at 20° -	$[\alpha]_D^{20} + 26{\cdot}5°$.
n_D 1·7432 at 10°	n_D^{10} 1·7432.
Per cent.	%.

ERRATA.

Vol. LXXXVIII (Abstr., 1905).

Part I.

Page	Line	
636	23	*for* "$NHBz{\cdot}[CH_2]_7{\cdot}NHBz$" *read* "$SO_2Ph{\cdot}NH{\cdot}[CH_2]_7{\cdot}NH{\cdot}SO_2Ph$."

Vol. XC (Abstr., 1906).

Part I.

181	5	*for* "*o*-methylcoumaric" *read* "*o*-methoxycinnamic."
402	5	,, "584" *read* "534."
979	3	,, "Krafft" *read* "Kraft."

Vol. LXXXIX (Trans., 1906).

1935	7*	*for* "one of the authors" *read* "the author."

Vol. XCI (Trans., 1907).

37	5	*for* "$O_2{:}C_6H_2Br_2{:}N_2$" *read* "$O{:}C_6H_2Br_2{:}N_2$."

---

* From bottom.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

XII.—The Optical Influence of Contiguity of Unsaturated Groups. By **Julius Wilhelm Brühl** (*continued*) . . . 121

XIII.—The Action of Acid Chlorides on Thioureas. By **Augustus Edward Dixon** and **John Hawthorne** 122

XIV.—Transformations of Highly Substituted Nitroaminobenzenes. II. *s*-Tribromo-1-nitroaminobenzene. By **Alice Emily Smith** and **Kennedy Joseph Previté Orton** . . 146

XV.—The Affinity Constants of Aminocarboxylic and Aminosulphonic Acids as determined by the aid of Methyl-orange. By **Victor Herbert Veley** 153

XVI.—Tetraketopiperazine. By **Alfred Theophilus de Mouilpied** and **Alexander Rule** 176

XVII.—Synthesis of Terebic, Terpenylic, and Homoterpenylic Acids. By **John Lionel Simonsen** (Schunck Research Fellow in the University of Manchester) 184

XVIII.—Preparation of Chromyl Dichloride. By **Herbert Drake Law** and **Frederick Mollwo Perkin** 191

XIX.—Benzoyl Derivatives of *N*-Methylsalicylamide. By **James McConnan** and **Morris Edgar Marples** 193

XX.—Disalicylamide. By **James McConnan** 196

XXI.—The Relation between Absorption Spectra and Optical Rotatory Power. Part I. The Effect of Unsaturation and Stereoisomerism. By **Alfred Walter Stewart** (Carnegie Research Fellow) 199

XXII.—Organic Derivatives of Silicon. Part II. The Synthesis of Benzylethylpropylsilicol, its Sulphonation, and the Resolution of the *dl*-Sulphonic Derivative into its Optically Active Components. By **Frederic Stanley Kipping** 209

XXIII.—Derivatives of Multivalent Iodine. Part II. Action of Heat on *p*-Iodoacetophenone Dichloride, *p*-Iodoacetanilide Dichloride, and on the Dichlorides derived from *o*-, *m*-, and *p*-Iodotoluene. By **William Caldwell** and **Emil Alphonse Werner** 240

XXIV.—The Condensation Products of Triacetic Lactone with Acetoacetic Ester and β-Aminocrotonic Ester. By **Frederick Noel Ashcroft Fleischmann**, M.A., Oxon. . 250

XXV.—Oxidation of Hydrocarbons of the Benzene Series. By **Herbert Drake Law** and **Frederick Mollwo Perkin** . 258

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Achelis, W., and F. Kutscher, ii, 114.
Agadschanianz, K., ii, 111.
Ageno, F. See M. G. Levi.
Aickelin, H. See O. Dimroth.
Albu, A., and C. Neuberg, ii, 115.
Alpers, K., i, 149.
Alvarez, E. P., ii, 132, 143.
Alway, F. J., ii, 126.
Anderlini, F. See R. Nasini.
André, G., ii, 122.
Angeli, A., and F. Angelico, i, 153.
Angelico, F., ii, 122.
Angelico, F. See also A. Angeli.
Arnold, V., ii, 115.
Arrivaut, G. See E. Vigouroux.
Arsonval, A. D'., and F. Bordas, ii, 71.
Auger, V., i, 109.
Azzarello, E., ii, 125.

B.

Bainbridge, F. A., ii, 113.
Balland, ii, 126.
Bamberger, E., and E. Kraus, i, 161.
Bamberger, E., and E. W. Remmert, i, 163.
Bamberger, E., and L. Rudolf, i, 122.
Bamberger, E., and S. Wildi, i, 164.
Bancroft, W. D., ii, 61.
Bang, I., ii, 136.
Barbier, P., and P. Sisley, i, 160.
Bardachzi, F., ii, 106.
Bargellini, G., and A. Mieli, ii, 77.
Batschinski, A., ii, 74.
Baudisch, O., i, 131.
Beatty, W. A. See P. A. Levene.
Beckenkamp, J. See W. E. Ford.
Beckmann, E., E. Bernhard, Eremie-Popa, and W. Gabel, ii, 71.
Bellucci, I., and N. Parravano, ii, 86, 87.
Bellucci, I., and S. Rubegni, ii, 94.
Berg, A., i, 146.
Berger, E., ii, 129.
Bernhard, E. See E. Beckmann.
Berthaud, J., i, 117.
Bertrand, G., ii, 136.
Bertrand, G., and Mlle. L. Rivkind, ii, 122.
Bertrand, G., and G. Weisweiller, ii, 120.
Beschke, E. See J. von Braun.
Billon, C., ii, 135.
Binet du Jassoneix, A., ii, 95.
Binning, S., and F. M. Perkin, i, 114.
Blanck, F. C. See J. B. Tingle.
Blankenberg, F. See F. Foerster.
Blanksma, J. J., i, 123, 126.
Bodenstein, M., and S. C. Lind, ii, 76.
Boetticher, H., ii, 138.
Bokorny, T., ii, 121.
Boltwood, B. B., ii, 62.
Bonamartini, G., ii, 138.
Bordas, F. See A. D'Arsonval.
Bottazzi, F., and G. d'Errico, i, 113.
Brachin, M., i, 128.
Brand, K., i, 119.
Braun, J. von, i, 110.
Braun, J. von, and E. Beschke, i, 123, 127.
Braun, J. von, E. Beschke, and C. Müller, i, 151.
Braun, J. von, and E. Schmitz, i, 105.
Breteau, P., and P. Woog, i, 105.
Briner, E., ii, 68.
Bruère, ii, 144.
Bruni, G., and B. L. Vanzetti, ii, 74.

Bruschi, D., ii, 124.
Bülow, C., and F. Busse, i, 165.
Busck, G., ii, 105.
Busse, F. See C. Bülow.
Bywaters, H. W., ii, 105.

C.

Caldwell, W., and E. A. Werner, Trans., 240.
Cambi, L. See M. Padoa.
Cameron, F. K., and H. E. Patten, ii, 126.
Carles, P., ii, 129.
Carlson, A. J., ii, 111.
Carlson, C. E., ii, 130.
Carlson, F., i, 116.
Carrăcido, J. R., ii, 131.
Carrasco, O., and M. Padoa, i, 152.
Carré, P., i, 142.
Carroll, C. G., ii, 75.
Cathcart, E. P., ii, 142.
Chavanne, G. See L. J. Simon.
Chavassieu, and A. Morel, ii, 135.
Chikashigé, M., ii, 88.
Chrustaleff, A., ii, 142.
Ciamician, G. L., and P. Silber, i, 119.
Ciusa, R., i, 137.
Clark, R. H., ii, 77.
Colomba, L., ii, 102.
Contardi, A. See G. Körner.
Cook, A. N., i, 126.
Cormimboeuf, H., and L. Grosman, ii, 138.
Cosyns, G., ii, 104.
Crismer, L., ii, 134.
Cushny, A. R., ii, 112.

D.

Dalebroux, Mdlle. R., and H. Wuyts, i, 105.
Demierre, H. See P. Dutoit.
Demolis, L., ii, 68.
Denzler, W. See F. Ullmann.
Dimroth, O., and H. Aickelin, i, 159.
Dixon, A. E., and J. Hawthorne, Trans., 122.
Dolezalek, F., and K. Finckh, ii, 87.
Dollfus, R., ii, 83.
Dorlencourt. See M. Tiffeneau.
Drews, A. See A. Michaelis.
Dufour, A., ii, 83.
Duke, W. W. See W. H. Howell.
Dumont, J., ii, 126.
Dutoit, P., and H. Demierre, ii, 75.
Dzierzgowsky, S. K. See W. S. Dzierzgowsky.
Dzierzgowsky, W. S., S. K. Dzierzgowsky, and N. O. Schumoff-Sieber, ii, 117.

E.

Ehrenberg, P. See T. Pfeiffer.
Ellinger, A., and C. Flamand, i, 153.
Eremie-Popa. See E. Beckmann.
Errico, G. d'. See F. Bottazzi.
Eve, A. S., ii, 62.
Ewan, T., i, 115.

F.

Fandre, A. See T. Klobb.
Fawsitt, C. E., ii, 66.
Feigl, J., ii, 118.
Filippi, F. de, ii, 109.
Finckh, K. See F. Dolezalek.
Fischer, F., ii, 72.
Fischer, H. See T. Zincke.
Flamand, C. See A. Ellinger.
Fleischmann, F. See F. Haber.
Fleischmann, F. N. A., Trans., 250.
Foerster, F., and F. Blankenberg, ii, 89.
Ford, W. E., and J. Beckenkamp, ii, 101.
Fosse, R., i, 136.
Foster, G. W. A. See F. Haber.
Frenkel-Heiden, ii, 110.
Freudenreich, E. von, and O. Jensen, ii, 120.
Freundler, P., i, 158.
Friedheim, C., and F. Keller, ii, 96.
Fritz, I. See H. Kauffmann.
Fröhlich, E. See E. Wedekind.
Fromherz, K., ii, 141.
Fühner, H., i, 150.

G.

Gabel, W. See E. Beckmann.
Gain, G., ii, 97.
Galimard, J., and L. Lacombe, ii, 121.
Gallagher, F. E., ii, 84.
Gamboa, R. L., ii, 103.
Gastine, G., ii, 137.
Gault, H., i, 147, 148.
Gautier, A., i, 134.
Genzken, U. See H. Strache.
Gin, G., ii, 92.

Glasmann, B., i, 109.
Glasser, E., ii, 101.
Goerens, P., and A. Stadeler, ii, 92.
Gooch, F. A., and M. A. Phelps, ii, 130.
Goodman, E. H., ii, 115.
Goutal, E., ii, 129.
Graf. See O. Ruff.
Graham, D. A. L. See G. G. Nasmith.
Grandmougin, E., i, 166.
Grandmougin, E., and H. Leemann, i, 163.
Grassi-Cristaldi, G., i, 114.
Green, W. V., i, 117.
Greshoff, M., ii, 121.
Grimmer, W., ii, 107.
Gröger, M., ii, 94.
Grosman, L. See H. Cormimboeuf.
Grossmann, H., and B. Schück, ii, 142.
Grün, A., i, 111.
Gülich, C. J., ii, 79.
Guertler, W., ii, 65.
Guillemard, H., ii, 141.
Guye, P. A., and G. Ter-Gazarian, ii, 80.

H.

Haber, F., ii, 67.
Haber, F., and F. Fleischmann, ii, 84.
Haber, F., and G. W. A. Foster, ii, 66.
Hahn, C., and A. Strutz, ii, 82.
Hahn, O., ii. 62.
Hamill, J. M., ii, 109.
Hammarsten, O., ii, 137.
Harvey, W. H., ii, 117.
Hauth, A. See A. Windaus.
Hawthorne, J. See A. E. Dixon.
Hedenström, A. von. See T. Zincke.
Heermann, P., ii, 132.
Heiduschka, A., ii, 72.
Heller. See O. Ruff.
Henle, F., i, 144, 161.
Henning, H. See M. Trautz.
Henry, L., i, 106.
Herissey, H., ii, 123.
Heydenreich, K., ii, 130.
Hidden, W. E., and C. H. Warren, ii, 103.
Hinricks, G. D., ii, 91.
Hinsberg, O., i, 124.
Hlawatsch, C., ii, 101.
Hörlein, H. See L. Knorr.
Hoffmann, J., ii, 82.
Hollard, A., ii, 83.
Holleman, A F., and J. Huisinga, i, 136.
Holleman, A. F., and H. A. Sirks, i, 131.
Holmberg, O., ii, 90.
Hopkins, F. G. See E. G. Willcock.
Horn, M. See E. Rupp.
Horner, O., ii, 118.
Houdard, M., ii, 92.
Howell, W. H., and W. W. Duke, ii, 110.
Hugounenq, L., i, 167.
Huisinga, J. See A. F. Holleman.

I.

Inclán, A. S., ii, 66.

J.

Jacoby, M., ii, 108.
Jaeger, F. M., ii, 78.
Jahoda, R. See H. Strache.
Jastrowitz, H., ii, 106.
Jensen, O. See E. von Freudenreich.
Jolles, A., ii, 135.
Jones, H. C., ii, 78.
Jonescu, D., i, 167; ii, 117.
Jost, F., ii, 95.

K.

Kablukoff, I. A. See W. F. Luginin.
Kaiserling, C., ii, 113.
Kauffmann, H., i, 127.
Kauffmann, H., and I. Fritz, i, 127.
Kelhofer, W., ii, 136.
Keller, F. See C. Friedheim.
Kellner, O., ii, 108.
Kempf, R., ii, 71.
Kipping, F. S., TRANS., 209.
Kirkness, J. M. See F. H. A. Marshall.
Kitagawa, F., and H. Thierfelder, i, 168.
Klobb, T., and A. Fandre, ii, 123.
Knoch. See O. Ruff.
Knorr, L., and H. Hörlein, i, 151.
Körner, G., and A. Contardi, 117, 118.
Kötz, A., and W. Zörnig, i, 111.
Kohler, E. P., i, 139.
Kondakoff, I. L., i, 144.
Konschegg, A., and H. Malfatti, ii, 93.
Kotelmann, P. See A. Michaelis.
Kraemer, A., i, 114.
Kraus, E. See E. Bamberger.
Kreidl, A., and A. Müller, ii, 107.

Künz, R., ii, 121.
Kuntze, W., ii, 72.
Kutscher, F., i, 114.
Kutscher, F. See also W. Achelis.

L.

Lacombe, L. See J. Galimard.
Laer, H. van, ii, 120.
Lamb, A. B. See A. Michael.
Lang, G., ii, 107.
Lavalle, F. P., ii, 136, 143.
Law, H. D., and F. M. Perkin, Trans., 191, 258.
Lazennec, I. See C. Moureu.
Leathes, J. B., ii, 114.
Leemann, H. See E. Grandmougin.
Léger, E., i, 151.
Lehmann, C., and W. Völtz, ii, 109.
Lehr, H. See C. Thomae.
Letulle, M., and Mlle. M. Pompilian, ii, 114.
Levene, P. A., and W. A. Beatty, i, 168.
Levene, P. A., and J. A. Mandel, i, 168.
Levi, M. G., and F. Ageno, ii, 69.
Levi, M. G., and E. Migliorini, ii, 81.
Liefman, E., and R. Stern, ii, 116.
Lind, S. C. See M. Bodenstein.
Löb, A., ii, 131.
Loeb, J., ii, 110, 113, 119.
Loewenstein, S., ii, 119.
Loewy, A., and C. Neuberg, ii, 115.
London, E. S., ii, 107.
London, E. S., and W. W. Polowzowa, ii, 108.
Lottermoser, A., ii, 78.
Luginin, W. F., and I. A. Kablukoff, ii, 72.
Lumière, A., L. Lumière, and A. Seyewetz, i, 124.
Lumière, L. See A. Lumière.
Luther, A., i, 128.

M.

McConnan, J., Trans., 196.
McConnan, J., and M. E. Marples, Trans., 193.
Maddocks, W. H. See L. G. Radcliffe.
Magri, G., ii, 64.
Malagnini, G. See E. Rimini.
Malfatti, H. See A. Konschegg.
Malfitano, G., and L. Michel, ii, 94.
Manaresi, A. See G. Plancher.
Manchot, W., and K. Zechentmayer, ii, 93.
Mandel, J. A. See P. A. Levene.
Mann, E. A., and C. E. Stacy, ii, 134.
Marples, M. E. See J. McConnan.
Marquis, R., i, 123.
Marshall, F. H. A., and J. M. Kirkness, ii, 113.
Mayeda, M., ii, 106.
Mayer, P., ii, 117.
Meier, H., ii, 118.
Meyer, K., ii, 118.
Michael, A., and A. B. Lamb, i, 134.
Michaelis, A., A. Drews, and P. Kotelmann, i, 154.
Michaelis, L., and L. Pincussohn, ii, 78.
Micheels, H., ii, 124.
Michel, L. See G. Malfitano.
Mieli, A. See G. Bargellini.
Migliorini, E. See M. G. Levi.
Mitchell, W. A. See G. S. Woodhead.
Moissan, H., and T. Watanabe, ii, 84.
Moldenhauer, W., ii, 85.
Monckman, J., ii, 79.
Montagne, P. J., i, 140, 141.
Moody, S. E., ii, 131.
Moore, B., and H. E. Roaf, ii, 73.
Morel, A. See Chavassieu.
Moreland, W. H., ii, 127.
Morgenroth, J., and O. Rosenthal, ii, 119.
Moscati, G., ii, 118.
Moulpied, A. T. de, and A. Rule, Trans., 176.
Moureu, C., and I. Lazennec, i, 159.
Müller, A. See A. Kreidl.
Müller, C. See J. von Braun.
Müller, M., ii, 111.
Müller, W. See H. Wedding.
Muller, J. A., ii, 131.
Muñoz del Castillo, J., ii, 62, 63, 64.

N.

Nasini, R., and F. Anderlini, ii, 61, 81.
Nasmith, G. G., and D. A. L. Graham, ii, 118.
Neuberg, C. See A. Albu.
Neuberg, C. See also A. Loewy.

O.

O'Hehir, C. J., ii, 120.
Oliver, A. M., ii, 62.

Orloff, N. A., ii, 89, 90.
Orton, K. J. P. See Miss A. E. Smith.
Ostromisslensky, I. von, i, 120.

P.

Paal, C., and E. Weidenkaff, i, 131.
Padoa, M., and L. Cambi, ii, 86.
Padoa, M., and U. Ponti, i, 146.
Padoa, M. See also O. Carräsco.
Pannertz, P., ii, 128.
Parravano, N. See I. Bellucci.
Pastureau, i, 113.
Patten, H. E. See F. K. Cameron.
Pellet, H., ii, 139.
Penfield, S. L., and F. C. Stanley, ii, 102.
Perciabosco, F. See F. Scurti.
Perkin, F. M. See S. Binning; H. D. Law.
Peters, A. W., ii, 121.
Pewsner, M., ii, 106.
Pfeiffer, T., P. Ehrenberg, and E. Reichenbach, ii, 126.
Pflüger, E., ii, 137.
Phelps, M. A. See F. A. Gooch.
Pierron, P., i, 121.
Pincussohn, L. See L. Michaelis.
Plancher, G., and A. Manaresi, ii, 125.
Plancher, G., and C. Ravenna, i, 152.
Plimmer, R. H. A., ii, 108
Polowzowa, W. W. See E. S. London.
Pompilian, Mlle. M. See M. Letulle.
Ponti, U. See M. Padoa.
Porcher, C., ii, 117.
Pribram, E., ii, 111.
Pribram, H., ii, 105.

Q.

Quensel, P. D., ii, 101.

R.

Radcliffe, L. G., and W. H. Maddocks, ii, 140.
Rakowski, A., ii, 74.
Rakusin, M. A., ii, 139.
Ranwez, F., ii, 80.
Ravenna, C. See G. Plancher.
Reichard, C., ii, 142.
Reichardt, C. J., ii, 144.
Reichenbach, E. See T. Pfeiffer.
Remmert, E. W. See E. Bamberger.
Rengade, E., ii, 83.
Richardson, F. W., ii, 140.
Rimini, E., and G. Malagnini, ii, 81.
Rivkind, Mlle. L. See G. Bertrand.
Roaf, H. E. See B. Moore.
Robin, L., ii, 139.
Roeder, H. See J. Wohlgemuth.
Roozeboom, H. W. B., ii, 80.
Rosenthal, O. See J. Morgenroth
Rossi, F., and F. Scurti, ii, 125.
Rowell, H. W., ii, 133.
Rubegni, S. See I. Bellucci,
Rudolf, L. See E. Bamberger.
Ruer, R., ii, 99, 100.
Ruff, O., Graf, Heller, and Knoch, ii, 98.
Rule, A. See A. T. de Moulpied.
Rupp, E., and M. Horn, ii, 132.
Rutherford, E., ii, 63.
Rywosch, D., ii, 104.

S.

Sachs, F., ii, 117, 135.
Salkowski, E., ii, 114.
Savarè, M., ii, 111.
Scal, C. See G. Urbain.
Schittenhelm, A., and J. Schmid, ii, 109.
Schlicht, A., ii, 130.
Schmid, J. See A. Schittenhelm.
Schmitt, C., i, 112.
Schmitz, E. See J. von Braun.
Scholl, R., and W. Steinkopf, i, 116.
Schroeder, H., ii, 123.
Schück, B. See H. Grossmann.
Schulze, E., i, 114.
Schumoff-Sieber, N. O. See W. S. Dzierzgowsky.
Scott, F. H., ii, 129.
Scurti, F., ii, 122.
Scurti, F., and F. Perciabosco, ii, 124.
Scurti, F. See also F. Rossi.
Semmler, F. W., i, 145.
Senter, G., ii, 68.
Seyewetz, A. See A. Lumière.
Shrewsbury, H. S., ii, 140.
Silber, P. See G. L. Ciamician.
Simmer, A., i, 149.
Simon, L. J., and J. Chavanne, i, 110.
Simonsen, J. L., TRANS., 184.
Sirks, H. A. See A. F. Holleman.
Sisley, P. See P. Barbier.
Smith, Miss A. E., and K. J. P. Orton, TRANS., 146.
Smith, J. L., ii, 112.
Sollmann, T., ii, 110.
Sommelet, M., i, 107.
Stacy, C. E. See E. A. Mann.
Stadeler, A. See P. Goerens.

Stanley, F. C. See S. L. Penfield.
Steinkopf, W. See R. Scholl.
Stern, R. See E. Liefman.
Steudel, H., i, 168.
Stewart, A. W., TRANS., 199.
Strache, H., U. Genzken, and R. Jahoda, ii, 127.
Stritar, M. J., ii, 134.
Suida, W., ii, 112.
Strutz, A. See C. Hahn.
Szilard, B., ii, 97.

T.

Thierfelder, H. See F. Kitagawa.
Thomae, C., i, 138.
Thomae, C., and H. Lehr, i, 113, 138, 139.
Thomas, V., 117.
Ter-Gazarian, G. See P. A. Guye.
Tiffeneau, M., and Dorlencourt, i, 130.
Timmermans, J., ii, 75.
Tingle, J. B., and F. C. Blanck, i, 120.
Torrey, H. A., and J. E. Zanetti, i, 146.
Trautz, M., and H. Henning, ii, 73.
Trillat, A., ii, 125.
Trobridge, F. G., ii, 100.
Tsakalotos, D. E., i, 105.
Tschelinzeff, W., i, 106.
Tschirch, A., and M. Wolff, i, 145.
Tsvett, M., ii, 144.
Turrentine, J. W., ii, 81.

U.

Ullmann, F., and W. Denzler, i, 142.
Urano, F., ii, 111.
Urbain, G., and C. Scal, ii, 61.

V.

Vamvakas, J., ii, 137.
Vandevelde, A. J. J., i, 168.
Vanzetti, B. L. See G. Bruni.
Veley, V. H., TRANS., 153; ii, 76.
Vernon, H. M., ii, 111.
Vigouroux, E., ii, 82, 88, 89, 95.
Vigouroux, E., and G. Arrivaut, ii, 97.
Vintilesco, J., ii, 123.
Völtz, W. See C. Lehmann.
Vorländer, D., ii, 70.

W.

Warren, C. H., ii, 133.
Warren, C. H. See also W. E. Hidden.
Watanabe, T. See H. Moissan.
Wedding, H., and W. Müller, ii, 93.
Wedekind, E., i, 137.
Wedekind, E., and E. Fröhlich, i, 122.
Weehuizen, P., ii, 142.
Weerman, R. A., i, 132.
Weidenkaff, E. See C. Paal.
Weisweiller, G. See G. Bertrand.
Weitzenböck, R., i, 167.
Werner, E. A. See W. Caldwell.
Weyl, T., i, 118.
Wigand, A., ii, 70.
Wildi, S. See E. Bamberger.
Willcock, E. G., and F. G. Hopkins, ii, 109.
Windaus, A., and A. Hauth, i, 129.
Wohlgemuth, J., ii, 107, 116.
Wohlgemuth, J., and H. Roeder, ii, 106.
Wolff, M. See A. Tschirch.
Woodhead, G. S., and W. A. Mitchell, ii, 113.
Woog, P. See P. Breteau.
Wulff, G., ii, 83.
Wuyts, H. See Mdlle. R. Dalebroux.

Z.

Zanetti, J. E. See H. A. Torrey.
Zechentmayer, K. See W. Manchot.
Zengelis, C., ii, 128.
Zeynek, R. von., i, 167.
Zincke, T., and H. Fischer, i, 132.
Zincke, T., and A. von Hedenström, i, 124.
Zörnig, W. See A. Kötz.

ERRATA.

VOL. LXXXVI (ABSTR., 1904).

PART I.

Page	Line	
222	15	*for* "$CR_2{:}CH_2{\cdot}OX \rightarrow CR_2{:}CH_2{\cdot}OH$" *read* "$CR_2{:}CH{\cdot}OX \rightarrow CR_2{:}CH{\cdot}OH$."

VOL. XCII (ABSTR., 1907).

PART I.

8	18	*for* "ARBASOFF" *read* "ARBUSOFF."
11	10*	,, "BARTELL" *read* "BARTELT."

Part II.

117	14	*for* "Dziergowsky" *read* "Dzierzgowsky."

VOL. LXXXIX (TRANS., 1906).

1567	12	*for* "orthosilicate" *read* "metasilicate."
1568 *et seq.*		,, "Scherer" *read* "Scheerer."
1569	12	,, "Chautelope" *read* "Chantelope."
1569	16	,, "Zi" *read* "Zr."

---

* From bottom.

remained constant. It was, however, not possible to obtain the two limonenes of quite equal rotatory power, that of *l*-limonene remaining a little lower. It seems, according to the opinion of Messrs. Schimmel and Co., that *l*-limonene is accompanied by some other constituent not separable by fractional distillation. This view was confirmed by the fact that a mixture of equal weights of *d*-limonene ($a_D + 104°15'$) and *l*-limonene ($a_D - 101°30'$), which have the same specific gravities ($d_4^{21} = 0·8402$ and $d_4^{20·5} = 0·8407$), does not display a rotatory power equal to the difference $+104°15' - 101°30' = +2°45'$, but that the rotation was actually found to be $+1°29'$, the mixture having again a practically unchanged specific gravity ($d_4^{20·85} = 0·8402$). As there is no other method of purifying the limonenes except by fractional distillation, the two samples prepared by Schimmel and Co. were used directly for my purpose. I am obliged to my colleague Prof. A. Klages, and Mr. F. Sommer for making the measurements.

Four series of determinations were made: (1) on *d*-limonene, (2) on *l*-limonene, (3) on a mixture of equal weights of both, and (4) on a mixture obtained by adding to *d*-limonene so much of the *l*-compound that the deviation in the polarimeter became inappreciable.

TABLE.

I.	*d*-Limonene, b. p. (corr.) 175·5—176°/763 mm.	$a_D^{19·5°} = +104°15'$
II.	*l*-Limonene, b. p. (corr.) 175·5—176·5°/763 mm.	$a_D^{19·5°} = -101°30'$
III.	Mixture of equal weights of *d*- and *l*-limonene, b. p. (corr.) 175·5—176·5°/763 mm.	$a_D^{19°} = +\ 1°29'$
IV.	*l*-Limonene added to *d*-limonene until the mixture became inactive, b. p. (corr.) 175·5—176·5°/763 mm.	$a_D^{20°} = \pm\ 0°00'$

			n.			
	$t°$.	d_4^t.	H_α.	*D*.	H_β.	H_γ.
I.	21·0°	0·8402	1·47124	1·47428	1·48223	1·48886
II.	20·5	0·8407	1·47157	1·47468	1·48256	1·48924
III.	20·7	0·8409	1·47143	1·47448	1·48239	1·48904
IV.	20·85	0·8402	1·47134	1·47443	1·48231	1·48898

	$\frac{n^2-1}{(n^2+2)d}$.			
	H_α.	*D*.	H_β.	H_γ.
I.	0·3328	0·3347	0·3395	0·3434
II.	0·3328	0·3347	0·3394	0·3434
III.	0·3327	0·3345	0·3393	0·3433
IV.	0·3329	0·3348	0·3395	0·3435

	$\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{d}$.				
	H_α.	*D*.	H_β.	H_γ.	$H_\gamma - H_\alpha$.
I.	45·26	45·51	46·17	46·71	1·45
II.	45·26	45·52	46·16	46·71	1·45
III.	45·24	45·49	46·14	46·68	1·44
IV.	45·27	45·53	46·17	46·72	1·45
Theory for $C_{10}H_{16}\,|^{=}_{2}$	44·97	45·24	—	46·40	1·43

On reference to the table, it is seen that the agreement between *d*- and *l*-limonene is so excellent that the amount of heterogeneous constituents in *l*-limonene must be but very small. There is further a very close accordance between the theoretical values and those observed for the molecular refraction and an almost absolute agreement as regards molecular dispersion.

My numbers are also in satisfactory harmony with the figures given by Sir W. H. Perkin for dipentene; mine are a little higher for molecular refraction, and somewhat lower for molecular dispersion.

The main result of these determinations is the fact that *d*- and *l*-limonene and their inactive mixture (dipentene) display, except in rotatory power, almost absolutely equal constants in every respect: in boiling point, specific gravity, refractive indices for every wave-length, specific and molecular refractions and dispersions within the whole visible spectrum.

Since *d*- and *dl*-$\Delta^{3.8(9)}$-*p*-menthadiene, prepared by Kay and Perkin, show remarkable differences in these physical constants, it is obvious that their relation cannot be the same as that of *d*- and *l*-limonene on the one hand and dipentene on the other. Therefore *dl*-$\Delta^{3.8(9)}$-*p*-menthadiene is probably a racemic compound—if the properties are not altered during its preparation (boiling with potassium hydrogen sulphate). At present it seems more likely that the difference in the optical behaviour of this *dl*-compound is due to racemisation and not to chemical change (conversion into terpenes of another kind), as the magnetic rotation of *d*- and *dl*-$\Delta^{3.8(9)}$-*p*-menthadiene displays but slight differences. A decisive conclusion, however, in this very interesting question can only be arrived at by preparing the *dl*-compound avoiding treatment with potassium hydrogen sulphate and by redetermination of its physical properties.

HEIDELBERG.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

XXV.—Oxidation of Hydrocarbons of the Benzene Series. By **Herbert Drake Law** and **Frederick Mollwo Perkin** (*continued*) 261

XXVI.—The Condensation of Salicylamide with Aryl Aldehydes. By **Charles Alexander Keane** and **William Walter Scott Nicholls** 264

XXVII.—The Condensation of Diethylmalonamide with Aldehydes. By **Harry Burrows** and **Charles Alexander Keane** 269

XXVIII.—The Constitution of Umbellulone. Part II. The Reduction of Umbellulonic Acid. By **Frank Tutin** . 271

XXIX.—The Reduction of Hydroxylaminodihydroumbellulone-oxime. By **Frank Tutin** 275

XXX.—Some Constituents of Natural Indigo. Part I. By **Arthur George Perkin** and **W. Popplewell Bloxam** . 279

XXXI.—The Alkylation of *d*-Fructose. By **Thomas Purdie**, F.R.S., and **David McLaren Paul**, B.Sc., Carnegie Scholar 289

XXXII.—Studies on Optically Active Carbimides. Part V. The Aryl Esters and the Amides of 1-Menthylcarbamic Acid. By **Robert Howson Pickard** and **William Oswald Littlebury** 300

XXXIII.—Note on the Arsenates of Lead and Calcium. By **Spencer U. Pickering**, M.A., F.R.S. 307

XXXIV.—The Absorption Spectra of Phthalic, *iso*Phthalic, and Terephthalic Acids, Phthalic Anhydride, and Phthalimide. By **Walter Noel Hartley** and **Edgar Percy Hedley** . 314

XXXV.—The Absorption Spectra of Benzoic Acid, the Benzoates, and Benzamide. By **Walter Noel Hartley** and **Edgar Percy Hedley** 319

XXXVI.—A Reaction of certain Colouring Matters of the Oxazine Series. By **Jocelyn Field Thorpe** 324

XXXVII.—The Alkaloids of Ergot. By **George Barger** and **Francis Howard Carr** 337

PAGE

XXXVIII.—$\alpha\alpha\gamma$-Trimethyl- and $\alpha\alpha\gamma\gamma$-Tetramethyltricarballylic Acids and $\alpha\gamma$-Dimethylbutane-$\alpha\beta\delta$-tricarboxylic Acid. By HERBERT HENSTOCK and CHARLES HENRY GRAHAM SPRANKLING 354

XXXIX.—Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part VI. The Partially Methylated 4 : 6-Diamino-*m*-xylenes. By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT 360

XL.—Experiments on the Synthesis of the Terpenes. Part I. (*continued*). Direct Synthesis of Terpin from Ethyl *cyclo*Hexanone-4-carboxylate. By FRANCIS WILLIAM KAY and WILLIAM HENRY PERKIN, jun. 372

XLI.—The Rapid Electroanalytical Deposition and Separation of Metals. Part I. The Metals of the Silver and Copper Groups and Zinc. By HENRY JULIUS SALOMON SAND . . 373

XLII.—Derivatives of Naphthacenequinone. By WILLIAM HENRY BENTLEY, ARTHUR FRIEDL, FREDERICK THOMAS, and CHARLES WEIZMANN [with E. C. C. BALY and W. B. TUCK]. 411

XLIII.—Constituents of Natural Indigo. Part II. By ARTHUR GEORGE PERKIN 435

XLIV.—Association of Phenols in the Liquid Condition. By JOHN THEODORE HEWITT and THOMAS FIELD WINMILL . 441

XLV.—The Constitution of Hydroxyazo-compounds. By WILLIAM BRADSHAW TUCK 449

XLVI.—Resolution of Tetrahydro-*p*-toluquinaldine into its Optically Active Components. By WILLIAM JACKSON POPE and THOMAS CONSTANTINE BECK 458

XLVII.—Displacement of Halogens by Hydroxyl. I. The Hydrolytic Decomposition of Hydrogen and Sodium Monochloroacetates by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities. By GEORGE SENTER 460

XLVIII.—New Cerium Salts. By GILBERT T. MORGAN and EDWARD CAHEN 475

XLIX.—Experiments on the Synthesis of the Terpenes. Part X. Synthesis of Carvestrene and its Derivatives. By WILLIAM HENRY PERKIN, jun., and GEORGE TATTERSALL 480

L.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part IX. A New General Method for Studying Intramolecular Change. By THOMAS STEWART PATTERSON and ANDREW McMILLAN, M.A. 504

LI.—Camphor-β-sulphinic Acid and Camphorylsulphonium Bases. By SAMUEL SMILES and THOMAS P. HILDITCH . . 519

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abegg, R., ii, 151.
Abegg, R. See also P. Müller.
Abel, J. J., and W. W. Ford, ii. 192.
Aberson, J. H., ii, 169.
Acree, S. F., i, 258.
Aktiengesellschaft für Anilin-Fabrikation, i, 203.
Altmann, A., ii, 173.
Amar, J., ii, 145.
Anders, G. See W. Herz.
Andreasch, R., i, 233.
Arbusoff, A. E., i, 174.
Arnoldi, H. See K. A. Hofmann.
Aron, H., and F. Müller, i, 265.
Artmann, P., and A. Skrabal, ii, 196.
Anger, V., ii, 174.
Autonoff, N., ii, 190.

B.

Bach, A., i, 268.
Badische Anilin- & Soda-Fabrik, i, 202, 210, 224, 226, 263.
Bainbridge, F. A., and A. P. Beddard, ii, 189.
Baly, E. C. C., and W. B. Tuck, Trans., 426.
Bang, I., i, 266.
Barger, G., and F. H. Carr, Trans., 337.
Bartelt, K. See F. W. Semmler.
Beck, T. C. See W. J. Pope.
Becquerel, J., ii, 147.
Beddard, A. P. See F. A. Bainbridge.
Bentley, W. H., A. Friedl, F. Thomas, and C. Weizmann, Trans., 411.
Berblinger, H. See R. Scholl.
Berthelot, D., ii, 154, 155.
Berthelot, M., ii, 153.
Beschke. See M. Freund.
Bettendorff, A., ii, 172.
Beythien, A., and A. Friedrich, ii, 202.
Blaise, E. E., and M. Maire, i, 241.
Blanc, G., i, 220.
Bloxam, W. P. See A. G. Perkin, J. Q. Orchardson.
Blumenthal, H. See E. Fischer.
Bodenstein, M. See A. Stock.
Bödecker, F. See O. Wallach.
Bogdan, P., ii, 153.
Bokorny, T., ii, 184.
Boldyreff, W., ii, 185.
Borchardt, L., and F. Lange, ii, 188.
Borchers, E. See A. Hantzsch.
Borsche, W., and M. Feise, i, 242.
Brand, K., and E. Stohr, i, 206.
Brandt, H. See M. Busch.
Brunner, K., i, 240.
Büchner. E. H., ii, 149.
Bülow, C., and M. Deseniss, i, 252.
Bünz, R. See A. Gutbier.
Burrows, H., and C. A. Keane, Trans., 269.
Busch, H., and K. Goldenthal, i, 184.
Busch, M. and H. Brandt, i, 259.
Busz, K., ii, 182.

C.

Cahen, E. See G. T. Morgan.
Carapelle, E. See F. C. Palazzo.
Carles, P., ii, 195.
Carletti, O., ii, 202.
Carr, F. H. See G. Barger.
Cassella, L. & Co., i, 254.
Castoro, N., ii, 192.
Chablay, E., ii, 195.
Charrin, A., and Goupil, ii, 191.
Chemische Fabrik auf Aktien (vorm. E. Schering), i, 253.

Chevalier, J., ii, 193.
Clarke, L., i, 169.
Cohen, N. H., i, 211, 230.
Colman, J. See S. Gabriel.
Colson, A., ii, 177.
Curtius, T., A. Darapsky, and E. Müller, i, 262.

D

Dakin, H. D., and C. C. Ransom, ii, 189.
Dalmer, K., ii, 183.
D'Ans, J., ii, 168.
Darapsky, A. See T. Curtius.
Darzens, G., i, 178, 182.
Delépine, M. See C. Matignon.
Demjanoff, N. J., i, 174.
Dennis, L. M., and H. Isham, ii, 165.
Dennstedt, M., and F. Hassler, ii, 195.
Denstorff, O. See A. Hantzsch.
Deseniss, M. See C. Bülow.
Desparmet, E. See L. Meunier.
Diels, O., and G Meyerheim, i, 180.
Döbner, O., i, 203.
Döbner, O., and G. Schmidt, i, 204.
Doelter, C., ii, 166.
Doht, R. See M. Picha.
Dormaar, J. M. M., ii, 200.
Dorn, H. See A. Michaelis.
Dott, D. B., i, 230, 235.
Drabble, E., and H. Drabble, ii, 191.
Drabble, E., and M. Nierenstein, ii, 192.
Drabble, H. See E. Drabble.
Dumansky, A. V., ii, 175.
Duncan, J. B., ii, 200.

E.

Edie, E. S., and D. Spence, ii, 184.
Eggers, H. E., ii, 189.
Eisenlohr, F. See J. Sand.
Eissler, B., and A. Pollak, i, 183.
Ekbom, A., i, 180.
Ellis, H. R., ii, 160.
Ewald, W., ii, 184.

F.

Farbenfabriken vorm. Friedr. Bayer & Co., i, 195, 224, 226.
Farbwerke vorm. Meister, Lucius, & Brüning, i, 202, 232, 263, 264.
Feise, M. See W. Borsche.
Fetzer, K. See E. Wedekind.
Fischer, A., ii, 161.
Fischer, E., i, 192, 200; ii, 148.
Fischer, E., and H. Blumenthal, i, 191.
Fischer, F., and H. Marx, ii, 163.
Fischer, F., and K. Massenez, ii, 162.
Fonzes-Diacon, H., ii, 164.
Foote, H. W., ii, 173.
Foote, H. W., and L. H. Levy, ii, 173.
Ford, W. W. See J. J. Abel.
Foster, N. B., ii, 189.
Franke, A., M. Kohn, E. Thiel, and K. Zwiauer, i, 171.
Fredenhagen, C, ii, 146.
Freis, R., ii, 183.
Freund, M., and Beschke, i, 235.
Freund, M., and A. Wirsing, i, 254.
Freundler, P., i, 174.
Freundlich, H., ii, 155.
Fribourg, C. See H. Pellet.
Fried, W., i, 184.
Friedheim, C., and O. Nydegger, ii, 196.
Friedl, A. See W. H. Bentley.
Friedrich, A. See A. Beythien.
Fromherz, K., i, 186.
Fromherz, K., and W. Meegen, i, 232.
Funk, W., ii, 199.

G.

Gabriel, S., i, 214.
Gabriel, S., and J. Colman, i, 237.
Gault, H., i, 181.
Gelmo, P., and W. Suida, i, 231.
Goldenthal, K. See H. Busch.
Gomolka, F. See A. Stock.
Goupil. See A. Charrin.
Graftiau, J., ii, 196.
Grandmougin, E., i, 263; ii, 164.
Grindley, H. S., and H. S. Woods, ii, 187.
Grossman, H., ii, 148.
Gruner, P., ii, 149.
Guertler, W., and G. Tammann, ii, 174.
Guillemard, H., i, 197.
Gulewitsch, W., i, 264.
Guntz, A., ii, 167.
Gutbier, A., and R. Bünz, ii, 181.
Guthrie, C. C., and F. H. Pike, ii, 186.

H.

Haber, F., ii, 168.
Hagen, T. von der. See A. Michaelis.
Hall, L D. See G. T. Kemp.
Hâncu. See C. Mannich.
Hantzsch, A., and O. Denstorff, i, 233.
Hantzsch, A., E. Borchers, and N. Rosanoff, i, 207.
Harries, C., and P. Temme, i, 183.
Hartley, W. N., and E. P. Hedley, Trans., 314, 319.
Hartman, R. N. See A. Michael.
Hassler, F. See M. Dennstedt.
Hazewinkel, J. J., ii, 194.
Hedin, S. G., i, 267, 268.
Hedley, E. P. See W. N. Hartley.
Heimann, E. See P. Jannasch.
Heller, G., i, 261.
Hemmelmayr, F. von, i, 230.
Henle, F., i, 222.
Henrich, F., ii, 150, 182.
Henry, L., i, 206.
Henstock, H., and C. H. G. Sprankling, Trans., 354.
Hepner, H., i, 244.
Herz, W., and G. Anders, ii, 159.
Herzog, R. O., i, 267.
Hewitt, J. T., and T. F. Winmill, Trans., 441.
Heynemann, H. See A. Stock.
Hiendlmaier, H. See K. A. Hofmann.
Hilditch, T. P. See S. Smiles.
Hörlein, H. See L. Knorr.
Hörmann, P. See J. König.
Hofmann, K. A., H. Arnoldi, and H. Hiendlmaier, i, 196.
Holde, D., and F. Schwarz, i, 176.
Hove, T. van, i, 173.
Hoyer, E., ii, 192.
Hüfner, G. von, ii, 165.

I.

Inagaki, C., ii, 186.
Isham, H. See L. M. Dennis.
Iwanoff, L., ii, 191.

J.

Jackson, C. L., and R. D. MacLaurin, i, 223.
Jaeger, F. M., ii, 157.
Jänecke, E., ii, 167.
Jannasch, P., and E. Heimann, ii, 197, 201.
Jantsch, G. See A. Werner.
Jaquerod, A., and F. L. Perrot, ii, 166.
Jelínek, J. See E. Votoček.
Jenisch, G., i, 240.
Jodlbauer, A., and H. von Tappeiner, i, 267.
Jones, H. C., and H. S. Uhler, ii, 147.
Juliusberg, F., i, 219

K.

Kabacznik, A. See R. Scholl.
Kaestle, K. See J. Sand.
Kahn, H. M., ii, 166.
Kailan, A., ii, 158.
Kaufler, F., and W. Suchannek, i, 225.
Kay, F. W., and W. H. Perkin, jun., Trans., 372.
Keane, C. A., and W. W. S. Nicholls, Trans., 264.
Keane, C. A. See also H. Burrows.
Kemp, G. T., and L. D. Hall, ii, 187.
Kholodny, P. I., ii, 165.
Khotinsky, E. See A. Pictet.
Kinder, H., ii, 199.
Kinoshita, S., ii, 151.
Kirbach, H., i, 265.
Klercker, K. O. af., ii, 186.
Knoevenagel, E., i, 202.
Knoll & Co., i, 235, 236.
Knorr, L., and H. Hörlein, i, 235.
Koch, H., ii, 198.
König, J., and P. Hörmann, ii, 202.
Körner, T., ii, 161.
Kohn, M. See A. Franke.
Kohn, M., and F. Wenzel, i, 237.
Konowaloff, M. I., i, 203.
Konowaloff, M. I., K. Miller, and Timtschenko, i, 170.
Kossel, A., and H. Pringle, i, 266.
Krasnosselsky, T., i, 267.
Kremann, R., ii, 157.
Krimberg, R., i, 264.
Krogh, A., ii, 188.
Krüger, F., ii, 187.
Kruijs, M. J. van't, ii, 197.
Kühling, O., ii, 166.
Küttner, S., ii, 185.
Kurnakoff, S., and A. N. Kusnetzoff, ii, 171.
Kusnetzoff, A. N. See S. Kurnakoff.
Kusnetzoff, M. I., ii, 160.

L.

Laar, J. J. van, ii, 156.
Ladenburg, R., ii, 146.

Lambrecht, R., i, 257.
Lami, P., ii, 201.
Lange, F. See L. Borchardt.
Lasserre, A., ii, 203.
Lebeau, P., ii, 175.
Ledingham, J. C. G., ii, 190.
Lee, F. S., ii, 187.
Léger, E., i, 234.
Lendenfeld, H. von, i, 221.
Lespieau, R., i, 173.
Leuchs, H., and O. Splettstösser, i, 176.
Levene, P. A., and J. A. Mandel, i, 266.
Levin, M., ii, 150.
Levy, L. H. See H. W. Foote.
Lillie, R. S., ii, 183.
Littlebury, W. O. See R. H. Pickard.
Loeb, L., ii, 184.
Loimaranta, L., ii, 151.
Lorenz, R., and W. Ruckstuhl, ii, 152.
Lublin, J., i, 213.
Lusk, G., ii, 188.

M.

MacCallum, J. B., ii, 186.
MacLaurin, R. D. See C. L. Jackson.
McLeod, A. F., i, 172.
Macleod, J. J. R., ii, 184.
McMillan, A. See T. S. Patterson.
Magnus-Levy, A., i, 228.
Maire, M. See E. E. Blaise.
Manasse, A., ii, 201.
Mandel, J. A. See P. A. Levene.
Mannich, C., i, 205.
Mansfield, J. See R. Scholl.
Marchionneschi, M. See N. Tarugi.
Marck, J. L. B. van der, ii, 187.
Marckwald, W., ii, 182.
Margosches, B. M., i, 218.
Marx, H. See F. Fischer.
Massenez, K. See F. Fischer.
Mathews, A. P., ii, 183, 189.
Matignon, C., ii, 153.
Matignon, C., and M. Delépine, ii, 179.
Mayer, P., i, 183.
Meegen, W. See K. Fromherz.
Menschutkin, B. N., ii, 169.
Merck, E., i, 253.
Meunier, L., and E. Desparmet, i, 186.
Meyer, E. von, i, 214.
Meyer, G. C., ii, 197.
Meyer, H., i, 179, 241.
Meyer, L. F., and H. Rietschel, ii, 185.
Meyerheim, G. See O. Diels.
Michael, A., and R. N. Hartman, i, 170.
Michaelis, A., H. Dorn, T. von der Hagen, W. Rassmann, and H. Wrede, i, 246.
Michaelis, L., and P. Rona, ii, 204.
Micklethwait, F. M. G. See G. T. Morgan.
Milbauer, J., ii, 163.
Miller, K. See M. I. Konowaloff.
Milobendzki, T., ii, 199.
Morgan, G. T., and E. Cahen, Trans., 475.
Morgan, G. T., and F. M. G. Micklethwait, Trans., 360.
Müller, E., and F. Spitzer, ii, 174.
Müller, E. See also T. Curtius, H. Stobbe.
Müller, F. See H. Aron.
Müller, P., and R. Abegg, ii, 159.
Müller, W. See P. Rona.
Murlin, J. R., ii, 186.

N.

Nernst, W., ii, 153.
Neuberg, C., and N. Popowsky, i, 253.
Neuberg, C. See also E. Salkowski.
Neurath, G., i, 221.
Nicholls, W. W. S. See C. A. Keane.
Nierenstein, M. See E. Drabble.
Noon, L., ii, 190.
Nordström, G., ii, 152.
Nover, W., i, 262.
Nydegger, O. See C. Friedheim.

O.

Obermiller, J., i, 200.
Olie, J., jun., ii, 175, 176, 177.
Orchardson, J. Q., W. P. Bloxam, and S. H. Wood, ii, 203.
Orloff, N. A., ii, 171.
Orton, K. J. P., i, 205.

P.

Palazzo, F. C., and E. Carapelle, i, 195.
Pastureau, i, 185.
Patterson, T. S., and A. McMillan, Trans., 504.
Paul, D. M. See T. Purdie.
Pellet, H., and C. Fribourg, i, 185.
Perkin, A. G., Trans., 435.

Perkin, A. G., and W. P. Bloxam, Trans , 279.
Perkin, jun., W. H., and G. Tattersall, Trans., 480.
Perkin, jun., W. H. See F. W. Kay.
Perotti, R., ii, 191.
Perrot, F. L. See A. Jaquerod.
Peters, W., i, 221, 239.
Petrenko-Kritschenko, P., i, 220.
Petruschewsky, A., i, 268.
Pfeiffer, O., ii, 194.
Picha, M., R. Doht, and S. Weisl, i, 178.
Pickard, R. H., and W. O. Littlebury, Trans., 300.
Pickering, S. U., Trans., 307.
Pictet, A., and E. Khotinsky, i, 175.
Pike, F. H. See C. C. Guthrie.
Plahl, W., ii, 204.
Plotnikoff, W. A., ii, 152.
Poizat. See A. Seyewetz.
Pollak, A. See B. Eissler.
Pope, W. J., and T. C. Beck, Trans., 458.
Popowsky, N. See C. Neuberg.
Posner, T., i, 212.
Praxmarer, A., i, 216.
Pringle, H. See A. Kossel.
Purdie, T., and D. M. Paul, Trans., 289.
Puttkammer, G. See J. Tröger.

R.

Raikow, P. N., ii, 170, 171.
Ransom, C. C. See H. D. Dakin.
Raper, H. S., i, 266.
Rassmann, W. See A. Michaelis.
Reimann, G., ii, 183.
Reimer, C. L., i, 176.
Riedel, J. D., i, 254.
Rietschel, H. See L. F. Meyer.
Rinne, R., ii, 169.
Rohde, G. See G. Schultz.
Rona, P. See L. Michaelis.
Rona, P., and W. Müller, ii, 186.
Rosanoff, N. See A. Hantzsch.
Roth, H. See A. Wohl.
Ruckstuhl, W. See R. Lorenz.
Rupp, E., ii, 194.

S.

Sachs, A., ii, 182.
Salkowski, E., and C. Neuberg, ii, 188.
Salzbergwerk Neu-Stassfurt, i, 169.
Sand, H. J. S., Trans., 373.
Sand, J., and F. Eisenlohr, ii, 178, 179.
Sand, J., and K. Kaestle, ii, 178.
Scheel, K., ii, 145.
Scheuer, O. See W. Vaubel.
Schiff, H., i, 206.
Schindelmeiser, I., i, 229.
Schlotterbeck, F., i, 185.
Schmid, K. See Weinland.
Schmidt, G. See O. Döbner.
Scholl, R., and H. Berblinger, i, 257.
Scholl, R., H. Berblinger, and J. Mansfield, i, 256.
Scholl, R., A. Kabacznik, and W. Steinkopf, i, 256.
Scholl, R., and J. Mansfield, i, 255.
Schultz, G., G. Rohde, and F. Vicari, i, 244.
Schwarz, E., ii, 167.
Schwarz, F. See D. Holde.
Schweitzer, H. See A. Wohl.
Sckworzow, V., ii, 160.
Seitz, W., ii, 150.
Semmler, F. W., and K. Bartelt, i, 226.
Senter, G., Trans., 460.
Séverin, E., i, 217.
Seyewetz, A., and Poizat, ii, 162.
Siegfried, M., i, 265.
Simon, L. J., i, 241.
Skrabal, A. See P. Artmann.
Slator, A., ii, 191.
Smiles, S., and T. P. Hilditch, Trans., 519.
Soave, M., ii, 193.
Spence, D. See E. S. Edie.
Spitzer, F. See E. Müller.
Splettstösser, O. See H. Leuchs.
Sprankling, C. H. G. See H. Henstock.
Staněk, V., ii, 192.
Stark, J., ii, 147.
Steinkopf, W., ii, 161.
Steinkopf, W. See also R. Scholl.
Stobbe, H., i, 177.
Stobbe, H., and E. Müller, i, 178.
Stock, A., F. Gomolka, and H. Heynemann, ii, 180.
Stock, A., and M. Bodenstein, ii, 181.
Stoermer, R., i, 204, 252.
Stohr, E. See K. Brand.
Strauss, H., ii, 135.
Suchannek, W. See F. Kaufler.
Suida, W. See P. Gelmo.
Surenjanz, J. See L. Tschugaeff.
Svedberg, T., ii, 160.

T

Tammann, G. See W. Guertler.
Tappeiner, H. von. See A. Jodlbauer.
Tarugi, N., and M. Marchionneschi, ii, 198.
Tattersall, G. See W. H. Perkin, jun.
Temme, P. See C. Harries.
Thiel, E. See A. Franko.
Thomas, F. See W. H. Bentley.
Thomlinson, J. C., ii, 153.
Thorpe, J. F., Trans., 324.
Timtschenko. See M. I. Konowaloff.
Tingle, J. B., and L. F. Williams, i, 209.
Töth, J., ii, 197.
Traube, I., ii, 145.
Tröger, J., and G. Puttkammer, i, 263.
Tschelinzeff, W., i, 199.
Tschitschibabin, A. E., i, 204.
Tschugaeff, L., i, 185.
Tschugaeff, L., and J. Surenjanz, i, 187, 198.
Tsitschenko, V. E., i, 182.
Tuck, W. B., Trans., 449.
Tuck, W. B. See also E. C. C. Baly.
Tunmann, ii, 193.
Turner, H. J., ii, 162.
Tutin, F., Trans., 271, 275.

U.

Uhler, H. S. See H. C. Jones.
Urano, F., i, 192.
Ury, H., ii, 188.

V.

Vaubel, W., and O. Scheuer, ii, 203.
Vegesack, A. von, ii, 170.
Vernon, H. M., ii, 185.
Veselý, V. See E. Votoček.
Vesterberg, A., i, 213.
Vicari, F. See G. Schultz.
Vieweg, W. See H. Wichelhaus.
Vignon, L., i, 231.
Vigouroux, E., ii, 176.
Völtz, W., ii, 185.
Votoček, E., ii, 195.
Votoček, E., and J. Jelínek, i, 245.
Votoček, E., and V. Veselý, i, 243.

W.

Wagner, A., i, 233.
Wagner, H. W., ii, 196.
Wahl, A., i, 217.
Wallach, O, i, 220, 228, 229.
Wallach, O., and F. Bödecker, i, 227.
Wedekind, E., and K. Fetzer, ii, 175.
Weinland, and K. Schmid, i, 169.
Weisl, S. See M. Picha.
Weizmann, C. See W. H. Bentley.
Wenzel, F. See M. Kohn.
Werner, A., i, 189, 238; ii, 161.
Werner, A., and G. Jantsch, i, 188.
Wessely, L., ii, 198.
Wichelhaus, H., and W. Vieweg, i, 186, 232.
Wieland, H., i, 196.
Wilde, H., ii, 149.
Williams, L. F. See J. B. Tingle.
Windaus, A., i, 212.
Winmill, T. F. See J. T. Hewitt.
Wirsing, A. See M. Freund.
Wirte, J. P., ii, 194.
Wohl, A., and H. Roth, i, 170.
Wohl, A., and H. Schweitzer, i, 194.
Wohlgemuth, J., ii, 187.
Wood, S. H. See J. Q. Orchardson.
Woods, H. S. See H. S. Grindley.
Wrede, H. See A. Michaelis.

Z.

Zeleny A. See J. Zeleny.
Zeleny, J., and A. Zeleny, ii, 152.
Zemplén, G., ii, 155.
Zopf, W., i, 218.
Zwiauer, K. See A. Franke.

ERRATA.

Vol. XCII (Abstr., 1907).

Part II.

Page	Line	
144	17*	*for* "**Tabloid**" *read* "**Pellet.**"
144	15*	,, "tabloids" † *read* "compressed pellets."
144	1*	

---

* From bottom.

† "Tabloid" being a registered trade-mark may not be used.

stopped. The mixture, which had a strong odour of benzaldehyde, was now transferred to a round-bottomed flask and heated on the water-bath for about half an hour, when it was distilled in a current of steam. We found it always desirable to heat the mixture in this way before subjecting it to steam distillation in order that the reaction might be completed. When this was not done there was a tendency for the mixture to froth over when steam was passed into it.

The distillate was extracted with ether and the aldehyde converted into the hydrogen sulphite compound, in order to separate it from any unchanged toluene. On decomposing the hydrogen sulphite compound 24 per cent. of benzaldehyde was obtained.

When ice was not used and the toluene was added in small quantities at a time, taking care not to allow the temperature to rise above 35 to 40°, we never obtained more than about 18 per cent. of benzaldehyde.

II. *Manganese Peroxide.*—One hundred grams of commercial manganese peroxide (theory requires 83 grams MnO_2) were mixed in a lead vessel with 300 c.c. of sulphuric acid, sp. gr. 1·52, and then 50 grams of toluene added. The mixture was vigorously agitated for five hours. After heating on the water-bath and distilling with steam, only 0·5 per cent. of benzaldehyde was obtained.

The experiment was then repeated, taking, however, 100 grams of freshly precipitated manganese peroxide and agitating for 6·5 hours. In this case 5 per cent. of benzaldehyde was obtained.

III. *Chromyl Dichloride.*—One hundred and forty grams of chromyl dichloride were dissolved in 200 c.c. of chloroform and placed in a glass jar fitted with a glass stirrer, and surrounded by cold water. Forty grams of toluene were dissolved in twice its volume of chloroform and allowed to run slowly into the well-agitated solution of chromyl dichloride. When the whole of the toluene had been added, the mixture was agitated for half an hour longer (altogether two hours) and allowed to stand overnight. It was then transferred to a round-bottomed flask containing a little water, and sulphurous acid was carefully added in excess. During the addition of the sulphurous acid, the flask and its contents were gently agitated. The mixture was distilled with steam, the chloroform containing the dissolved aldehyde separated from the water, and the chloroform evaporated. The oily product was shaken with a concentrated solution of sodium hydrogen sulphite. The hydrogen sulphite compound was washed with ether to free it from any unchanged toluene and the aldehyde recovered in the usual manner. Yield of benzaldehyde, 44 per cent.

IV. *Persulphates.*—Two hundred grams of ammonium persulphate were mixed with 500 c.c. of 4*N*-sulphuric acid, and 2 grams of silver sulphate and 40 grams of toluene added. The top of the vessel was closed with a sheet of lead, through which passed a glass stirrer and a tube in connexion with a Kipp's apparatus for generating carbon dioxide. The mixture was vigorously agitated without cooling, so as to form an emulsion. The temperature rose to 45°; after seven hours, it had fallen to that of the atmosphere and the mixture was distilled with steam. The benzaldehyde was separated as usual by means of the hydrogen sulphite compound, the yield being 78 per cent.

With 2*N*-acid, the yield of aldehyde was poor.

p-*Xylene*.

Lead Peroxide.—Fifty grams of *p*-xylene were added to 300 c.c. of sulphuric acid, sp. gr. 1·52, and the mixture thoroughly agitated in an atmosphere of carbon dioxide. Two hundred and fifty grams of lead peroxide were then added in quantities of about 50 grams at one time, by which means the temperature of the mixture was kept at about 45°. The whole operation took about three hours. The mixture was then transferred to a flask and heated on the water-bath for about half an hour, after which it was distilled with steam. The yield of aldehyde was 27·5 per cent.

Manganese Peroxide.—Fifty grams of *p*-xylene were mixed so as to form an emulsion with 100 grams of manganese peroxide and 300 c.c. of sulphuric acid, sp. gr. 1·52. The mixing was continued for about six hours, during which time the temperature did not rise above 25°. The mixture was then heated on the water-bath for half an hour and distilled with steam. The yield of aldehyde was 14·5 per cent.

Chromyl Dichloride.—The preparation was exactly similar to that described under toluene, and the yield of aldehyde varied between 70 and 80 per cent.

Persulphate.—In this case, it was found essential to cool the mixture during the time the reaction was taking place. In one case, taking 40 grams of *p*-xylene, 190 grams of ammonium persulphate, 500 c.c. of 4*N*-sulphuric acid, and 2 grams of silver sulphate, the temperature at the commencement was 15°; in fifty minutes it had risen to 29°, and ten minutes later the mixture boiled over, the temperature having risen to 102°. When the above mixture was well agitated in an atmosphere of carbon dioxide, the vessel being placed in cold water so that the temperature did not rise above 25°, yields of *p*-tolualdehyde varying from 35 to 48 per cent. were obtained.

The methods of procedure with *o*- and *m*-xylene were similar to those employed for *p*-xylene; the yields obtained by the different processes of oxidation are tabulated on page 263. Mesitylene and ψ-cumene also behaved in a normal manner, but the yields of aldehyde were less than in the cases of the xylenes.

Cymene was found to be very difficult to oxidise, even when the temperature, in the case of oxidation with lead peroxide, manganese peroxide, and persulphates, was allowed to rise unchecked. This was from 40 to 50° in the case of the peroxides, using acid of sp. gr. 1·53. With persulphates the temperature, using 4*N*-acid, rose to about 35°. In this case the reaction showed a tendency to proceed beyond the aldehyde stage and a considerable quantity of cuminic acid was obtained, the yield of cuminaldehyde being very small. The aldehyde is probably first produced and then undergoes oxidation, for a considerable amount of unchanged cymene was always recovered.

Although the main product of oxidation of all the hydrocarbons was the mono-aldehyde, on working up the residues from a large number of experiments small quantities of the alcohols were obtained. The amounts, however, were so small that they certainly did not represent more than 0·1 per cent. of the hydrocarbon employed. At the same time the fact that these small quantities of alcohols are obtained would point to the probability that the alcohol is the first product, and that by further oxidation the aldehyde is formed. In some cases a considerable quantity of resin was produced, and this was particularly marked when persulphates were employed.

	Percentage yield of aldehydes with different oxidising agents.				
	Electrolytic oxidation.	Lead peroxide.	Manganese peroxide.	Persulphates.	Chromyl dichloride.
Toluene	10—20	18—24	5	78	44
o-Xylene	25—30	28	38	—	65
p-Xylene..	25—35	27·5	14·5	35—48	70—80
m-Xylene	10—15	20	—	44	60
Mesitylene	10—15	8·5	16	5·8	5·5
ψ-Cumene	10—12	11	17	—	5
Cymene	10, aldehyde 20, alcohols	10	1	0·5	8

It should also be mentioned that when the hydrocarbons were oxidised with chromyl dichloride, in some cases considerable quantities of chlorinated products were obtained. This was usually the case when the yield of aldehyde was small and was particularly noticeable with mesitylene and *m*-xylene.

The authors desire to express their thanks to the Committee of the Government Research Fund of the Royal Society for a grant which, in part, defrayed the expenses in connexion with this investigation.

Chemical Laboratory,
Borough Polytechnic Institute,
Borough Road, London.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

LI.—Camphor-β-sulphinic Acid and Camphorylsulphonium Bases. By Samuel Smiles and Thomas P. Hilditch (*continued*) 525

LII.—Derivatives of Multivalent Iodine. Part III. The Action of Heat on Iodobenzene Dichloride, and on the *m*- and *p*-Nitro- and *p*-Chloro-derivatives. By William Caldwell and Emil Alphonse Werner 528

LIII.—Depression of the Freezing Point of Aqueous Solutions of Hydrogen Peroxide by Potassium Persulphate and other Compounds. By Thomas Slater Price, D.Sc. 531

LIV.—The Reduction Products of *o*- and *p*-Dimethoxybenzoin. By James Colquhoun Irvine, Ph.D., D.Sc., and Agnes Marion Moodie, M.A., B.Sc., Carnegie Scholar 536

LV.—The Action of Ethylene Dibromide and of Propylene Dibromide on the Disodium Derivative of Diacetylacetone. By Alexander William Bain 544

LVI.—Volume Changes which Accompany Transformations in the System $Na_2S_2O_3 : 5H_2O$. By Harry Medforth Dawson and Colin Gyrth Jackson 552

LVII.—The Constitution of Chaulmoogric and Hydnocarpic Acids. By Marmaduke Barrowcliff and Frederick Belding Power 557

LVIII.—The Formation and Reactions of Imino-compounds. Part III. The Formation of 1 : 3-Naphthylenediamine and its Derivatives from *o*-Toluonitrile. By Ernest Francis Joseph Atkinson, Harry Ingham, and Jocelyn Field Thorpe 578

LIX.—The Velocity of Hydrolysis of Aliphatic Amides. By James Codrington Crocker, M.A. 593

PAGE

LX.—Interaction of Alkali Starch and Carbon Disulphide. Xanthogenic Esters of Starch. By **Charles Frederic Cross, Edward John Bevan**, and **John Frederic Briggs** . 612

Annual General Meeting 615

Presidential Address. 626

Obituary Notices 660

LXI.—The Hydrolysis of Amygdalin by Acids. By **Robert J. Caldwell**, B.Sc. (Lond.), Leathersellers' Company's Research Fellow, and **Stephen Lewis Courtauld**, B.A. (Cantab.) 666

LXII.—Mandelonitrile Glucosides. Prulaurasin. By **Robert J. Caldwell**, B.Sc. (Lond.), Leathersellers' Company's Research Fellow, and **Stephen Lewis Courtauld**, B.A. (Cantab.) 671

LXIII.—The Interaction of Ammonium Salts and the Constituents of the Soil. By **Alfred Daniel Hall**, M.A., and **Conrad Theodore Gimingham** 677

LXIV.—The Reduction of Carbon Dioxide to Formaldehyde in Aqueous Solution. By **Henry John Horstman Fenton** . 687

LXV.—An Extension of the Benzoin Synthesis. By **Reginald W. L. Clarke** and **Arthur Lapworth** 694

LXVI.—Studies in Optical Superposition. Part III. By **Thomas Stewart Patterson** and **John Kaye** 705

LXVII.—Influence of Non-electrolytes and Electrolytes on the Solubility of Sparingly Soluble Gases in Water. The Question of Hydrates in Solution. By **James Charles Philip** 711

LXVIII.—Organic Derivatives of Silicon. Part III. *dl*-Benzylmethylethylpropylsilicane and Experiments on the Resolution of its Sulphonic Derivative. By **Frederic Stanley Kipping** 717

LXIX.—Electrolytic Reduction. Part III. By **Herbert Drake Law** 748

LXX.—The Estimation of Small Quantities of Nitrogen Peroxide. By **Robert Robertson**, M.A., D.Sc., and **Sidney Scrivener Napper** 761

LXXI.—The Evolution of Nitrogen Peroxide in the Decomposition of Guncotton. By **Robert Robertson**, M.A., D.Sc., and **Sidney Scrivener Napper** 764

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Ackermann, D., and F. Kutscher.
Ahrens, F. B., i, 269.
Alba, F. See A. Hubert.
Alexandroff, A. See V. E. Tistshenko.
Alexéeff, D. W., ii, 239.
Alsberg, C. L. See R. Fitz.
Alsleben, P. See F. Sachs.
Alway, F. J., and G. R. McDole, ii, 294.
Ampola, G., and S. de Grazia, ii, 287.
Anderson, W. H., ii, 309.
André, G., ii, 288, 291.
Andrlík, K., ii, 293.
Angeli, A., and L. Marino, i, 321.
Angelico, F., i, 332.
Antonoff, S. N., and B. V. Malysheff, ii, 262.
Arbusoff, A. E., i, 275.
Aron, H., ii, 280.
Arrivaut, G. See E. Vigouroux.
Asher, L., and R. Rosenfeld, ii, 279.
Atkinson, E. F. J., H. Ingham, and J. F. Thorpe, Trans., 578.
Auger, V., ii, 263.
Autenrieth, W., and P. Mühlinghaus, i, 316.

B.

Badische Anilin- & Soda-Fabrik, i, 324, 327.
Baer, J., and L. Blum, ii, 285.
Bain, A. W., Trans., 544.
Bakscht, A. See H. Goldschmidt.
Barker, T. V., ii, 240.
Barkow, C. See E. Erlenmeyer, jun.
Barrowcliff, M., and F. B. Power, Trans., 557.
Battelli, A., and A. Stefanini, ii, 233.
Baubigny, H., ii, 301.
Bauer, H., and H. Moser, i, 307.
Bauer, R., ii, 310.
Baume, G., and D. E. Tsakalotos, ii, 227.
Baumstark, R. See M. Bönninger.
Baxter, G. P., ii, 265.
Baxter, G. P., C. H. Hickey, and W. C. Holmes, ii, 253.
Beck, K., and K. Ebbinghaus, ii, 232.
Beck, K., K. Ebbinghaus, and W. Treitschke, ii, 232.
Becker, W. See H. Lührig.
Beckmann, E., ii, 209.
Becquerel, H., ii, 213.
Beger, C. See A. Morgen.
Béhal, A., and M. Sommelet, i, 275, 282.
Behr, G. E. See T. W. Richards.
Berblinger, H. See R. Scholl.
Berkeley, Earl of, and E. G. J. Hartley, ii, 234.
Berl, E., and W. Smith, jun., i, 289.
Bernhart, K. See W. Koenigs.
Bernini, A., ii, 225.
Berthelot, M., ii, 215, 256.
Berthelot, M., and P. Landrieu, ii, 230.
Betti, M., i, 314.
Betti, M., and C. M. Mundici, i, 321.
Bevan, E. See C. F. Cross.
Bial, M., ii, 309.
Bickel, A., and L. Pincussohn, ii, 280.
Biginelli, P., ii, 317.
Biltz, H., and P. Herms, ii, 262.
Biltz, W., ii, 236.
Blaise, E. E., and H. Gault, i, 280, 332.
Blanck, E., ii, 295.
Block, W., ii, 222.
Bloemendal, W. H., ii, 288.
Blum, L. See J. Baer.
Bodmer, E. See E. Grandmougin.

Boedtker, E., ii, 277.
Bönninger, M., R. Baumstark, and L. Mohr, ii, 282.
Bogen, H., ii, 280.
Bogert, M. T., J. E. Sinclair, and J. D. Wiggin, i, 351.
Boltwood, B. B., ii, 220.
Böttcher, O., ii, 295.
Borsche, W., i, 326.
Boulez, V., ii, 306.
Bourquelot, E., and H. Hérissey, i, 330.
Bräunlich, F. See A. Werner.
Bragg, W. H., ii, 219.
Bredig, G., i, 372.
Briggs, J. F. See C. F. Cross.
Brill, O., ii, 233.
Brink, F. N. See T. W. Richards.
Bronson, H. L., ii, 216.
Brugsch, T., and R. Hirsch, ii, 284.
Brunner, E., ii, 223.
Brunner, K., i, 319.
Buch, K., ii, 261.
Bucherer, H. T., and F. Seyde, i, 344.
Bülow, C., and M. Lobeck, i, 301.
Bürgi, E., i, 302; ii, 286.
Buisson, A., ii, 306.
Burr. See H. Kauffmann.
Busch, M., and E. Meussdörffer, i, 347.

C.

Caldwell, R. J., and S. L. Courtauld, Trans., 666, 671.
Caldwell, W., and E. A. Werner, Trans., 528.
Campbell, N. R., and A. Wood, ii, 217.
Carles, P., ii, 282.
Carpi, U. See J. Morgenroth.
Carse, G. A., and T. H. Laby, ii, 236.
Cassella, L. & Co., i, 347, 364.
Charabot, E., and G. Laloue, ii, 290.
Charitschkoff, K. W., i, 269.
Chemische Fabrik Uerdingen Lienau & Co., i, 328.
Chocenský, K. See J. Stoklasa.
Clapp, S. H. See T. B. Osborne.
Clarke, R. W. L., and A. Lapworth, Trans., 694.
Coates, J. E., ii, 257.
Cobellis, F. See A. Piutti.
Colson, A., ii, 267.
Comanducci, E., ii, 311.
Coppadoro, A., ii, 324.
Coppalle, A., ii, 302.
Courtauld, S. L. See R. J. Caldwell.
Crocker, J. C., Trans., 593.
Cross, C. F., E. Bevan, J. F. Briggs, Trans., 612.
Curtius, T., A. Darapsky, and E. Müller, i, 359.
Cuthbertson, C., and E. P. Metcalfe, ii, 205.
Czerkis, M., i, 331.

D.

Dakin, H. D., ii, 320.
Darapsky, A. See T. Curtius.
Darzens, G., i, 277.
Dawe, K. See A. Werner.
Dawson, H. M., and C. G. Jackson, Trans., 552.
Dennis, L. M., and H. Isham, ii, 255.
Deussen, E., and H. Kessler, ii, 265, 298.
Deventer, C. M. van, ii, 265.
Dewar, Sir J., and H. O. Jones, ii, 266.
Dimaré, V., ii, 285.
Dons, R. K., ii, 314.
Drucker, K., ii, 225.
Durrant, R. G., ii, 234.

E.

Ebbinghaus, K. See K. Beck.
Edmunds, C. W., ii, 279.
Eisenkolbe, P. See A. Köhler.
Eisner, F. See O. Ruff.
Ellis, H. R., ii, 270.
Emich, F., and J. Donau, ii, 296.
Emmert, B., i, 339.
Emster, K. van, ii, 253.
Engler, C., and H. Sieveking, ii, 218.
Ensrud, G., ii, 249.
Eppinger, H., ii, 286.
Erlandsen, A., i, 371.
Erlenmeyer, jun., E., C. Barkow, and O. Herz, i, 318.
Ernest, A. See J. Stoklasa.
Exner, F., and E. Haschek, ii, 209.

F.

Faber, P., ii, 305.
Fahrion, W., i, 329.
Fanto, R., and M. J. Stritar, i, 277.

Farbenfabriken vorm. Friedr. Bayer & Co., i, 361.
Farbwerke vorm. Meister, Lucius & Brüning, i, 312, 355, 362, 363.
Farr, E. H., and R. Wright, ii, 318.
Faworsky, A. E., i, 274.
Fenton, H. J. H., TRANS., 687; ii, 308.
Finger, H., i, 298.
Fischer, E., and A. Schulze, i, 295.
Fischer, F., and K. Massenez, ii, 254.
Fischer, O., i, 352.
Fitz, R., C. L. Alsberg, and L. J. Henderson, ii, 284.
Florence, ii, 317.
Flury, F. See A. Gütbier.
Fournier, A., ii, 305.
Fournier, H., i, 271.
Foster, W. H., ii, 303.
Frabot, C. See F. Jean.
Fränkel, S., i, 369.
Frank, P. See A. Rosenheim.
Franke, A., i, 286.
Franklin, E. C., ii, 264.
Fraps, G. S., ii, 314.
Freundler, P., i, 285.
Frey, E. See H. Kionka.
Frey, O., i, 331.
Friedländer, P., and G. Müller, i, 334.
Fritsch, R. See E. Lippmann.
Fröhlich, E., i, 346.
Fürth, O. von, i, 368.

G.

Galli, G., ii, 303.
Gandolfo, D. See A. Piutti.
Ganassini, D., ii, 313.
Gault, H. See E. E. Blaise.
Gifford, J. W., ii, 205.
Gimingham, C. T. See A. D. Hall.
Godchot, M., i, 308.
Godchot, M. See also E. Jungfleisch.
Goldschmidt, H., and A. Bakscht, ii, 244.
Goldschmidt, H., and V. Scholz, ii, 244.
Goldschmiedt, G., i, 310.
Goldstein, J. See J. Pollak.
Grandmougin, E., i, 362.
Grandmougin, E., and E. Bodmer, i, 355.
Grassi, U., ii, 217.
Grazia, S. de. See G. Ampola.
Greifenhagen, H. See R. von Walther.
Grignard, V., and J. Reif, i, 287.
Grigoréeff, A. A. See V. E. Tistshenko.
Grigoréeff, G. N. See V. E. Tistshenko.
Grimal, E., i, 329.
Grossman, H., ii, 303.
Grübler, ii, 316.
Guillemard, H., i, 300.
Gulewitsch, W. von, i, 337.
Gushoff, M. See V. E. Tistshenko.
Gutbier, A., and F. Flury, ii, 255.
Gutbier, A., and H. Zwicker, i, 289.
Gutmann, A., ii, 298.
Guttmann, A. See W. Herz.

H.

Haitinger, L. See V. von Lang.
Halban, H. von, ii, 246.
Hall, A. D., and C. T. Gimingham, TRANS., 677.
Haller, A., and C. Weimann, i, 278.
Hammarsten, O., and E. Pflüger, ii, 309.
Hanriot, M. ii, 292.
Hardy, W. B. See Miss E. G. Willcock.
Hartley, E. G. J. See the Earl of Berkeley.
Hartley, W. N., ii, 210.
Hascheck, E. See F. Exner.
Hassreidter, V., ii, 301.
Hauser, O., ii, 273.
Heinze, B., ii, 295.
Heller, W. See O. Ruff.
Henderson, L. J. See R. Fitz.
Henrich, F., Raab, and Ruppenthal, i, 323.
Henry, L., i, 273.
Henzr, M., i, 370.
Hérissey, H. See E. Bourquelot.
Herms, P. See H. Biltz.
Hertzmann, J. See A. Rosenheim.
Herz, O. See E. Erlenmeyer.
Herz, W., and A. Guttmann, ii, 274.
Herzog, R. O., ii, 312.
Hickey, C. H. See G. P. Baxter.
Hildebrandt, H., ii, 298.
Hiltner, L., and L. Peters, ii, 296.
Hinrichs, G., i, 269.
Hirsch, R. See T. Brugsch.
Hodgson, T. R., ii, 315.
Hoff, J. H. van't. See W. Meyerhofer.
Holleman, A. F., and G. L. Voerman, i, 334.
Holmes, W. C. See G. P. Baxter.
Honcamp, F., ii, 293.
Honcamp, F. See also A. Köhler.

Hotz, G., ii, 285.
Hubbard, J. L. See T. W. Phelps.
Hubert, A., and F. Alba, ii, 299.
Hutchins, jun., E. B., and V. Lenher, ii, 274.
Hutchinson, A., ii, 277.

I.

Ibele, J. See W. Koenigs.
Ingham, H. See E. F. J. Atkinson.
Irvine, J. C., and A. M. Moodie, Trans., 536.
Isham, H. See L. M. Dennis.

J.

Jackson, C. G. See H. M. Dawson.
Jaeger, F. M., ii, 315.
Jänecke, E., ii, 264, 278.
Janson, A. von., i, 312.
Jean, F., and C. Frabot, ii, 320.
Jermakoff, W. W., ii, 294.
Jörgensen, G., ii, 312.
Johns, C., ii, 257.
Jolles, A., ii, 309.
Jones, H. C., and H. S. Uhler, ii, 211, 212.
Jones, H. O., ii, 237.
Jones, H. O. See also Sir J. Dewar.
Jungfleisch, E., and M. Godchot, i, 279.

K.

Kaas, K. See Z. H. Skraup.
Kailan, A., ii, 242, 243.
Kalle, & Co., i, 276, 313, 320, 362, 363, 370.
Kastner, J. See E. Votoček.
Kauffmann, H., ii, 214.
Kauffmann, H., and Burr, ii, 215.
Kaufler, F., i, 507.
Kaye, J. See T. S. Patterson.
Kayser, E., and H. Marchand, ii, 288.
Kehrmann, F., and A. Winkelmann, i, 345.
Kelvin, Lord, ii, 216.
Kessler, H. See E. Deussen.
Kimpflin, G., ii, 389.
Kipper, H. B. See H. A. Torrey.
Kipping, F. S., Trans., 717.
Kionka, H., and E. Frey, ii, 285.
Kirkby, P. J., ii, 221.
Klostermann, W. See T. Zincke.
Klut, ii, 275.
Köhler, A., F. Honcamp, and P. Eisenkolbe, ii, 282.
Koenigs, W., K. Bernhart, and J. Ibele, i, 345.
Kohlschütter, V., and M. Kutscheroff, ii, 267.
Kohn, M., i, 338.
Kohn, S., and L. Wessely, ii, 300.
Kohn-Abrest, E., ii, 313.
Kondakoff, T. L., and T. Schindelmeiser, i, 329.
Konowaloff, M. T., i, 271, 279.
Korselt, J. See F. Ullmann.
Korten, F. See E. Rimbach.
Kost, J. See E. Rupp.
Kostanecki, S. von., and V. Lampe, i, 334.
Krafft, P. See H. Ley.
Kremann, R., i, 311; ii, 241.
Kreutzer, C. See A. Werner.
Krull, B., ii, 316.
Kučera, B., ii, 219.
Künzel, A. See R. Scholl.
Kutscher, F. See D. Ackermann.
Kutscher, F., and A. Lohmann, ii, 284.
Kurnakoff, N. S., and N. A. Pushin, ii, 262.
Kutscher, F., i, 337.
Kutscheroff, M. See V. Kohlschütter.

L.

Laar, J. J. van., ii, 228.
Laby, T. H. See G. A. Carse.
Läwen, A., ii, 286.
Laloue, G. See E. Charabot.
Lampe, V. See S. von Kostanecki.
Landini, G., ii, 208.
Landrieu, P. See M. Berthelot.
Lang, V. von, and L. Haitinger, ii, 264.
Lantelme, E. See A. Naumann.
Lapworth, A. See R. W. L. Clarke.
Law, H. D., Trans., 748.
Lawroff, D., ii, 280.
Lebeau, P., ii, 264.
Léger, E., i, 336.
Lehmann, E., ii, 434.
Lemoine, G., ii, 248.
Lenher, V. See E. B. Hutchins.
Lenher, V., and H. B. North, ii, 255.
Lenher, V., and E. Wolesensky, ii, 255.
Lenoble, E., ii, 300.
Levene, P. A., and C. A. Roniller, ii, 319.
Levin, M., ii, 220.
Lewkonja, K., ii, 261.
Ley, H., and P. Krafft, i, 301.
Ley, H., and F. Werner, i, 302.

Lifschütz, T., i, 315.
Lindenbaum, E. See A. Naumann.
Lippmann, E., and R. Fritsch, i, 309.
Lobeck, M. See C. Bülow.
Lockemann, G., ii, 250.
Loeb, L., ii, 279.
Loeb, O., and L. Michaud, ii, 285.
Loevenhart, A., ii, 281.
Loevenhart, A. S., and G. Peirce, ii, 281.
Loevenhart, A., and C. G. Souder, ii, 281.
Lohmann, A. See F. Kutscher.
Lohmeyer, J., ii, 211.
Long, J. H., i, 367.
Low, W. H., ii, 304.
Lührig, H., and W. Becker, ii, 303.
Lukomnik, J., i, 371.
Lury, R. E. de., ii, 247.

M.

McCrea, R. H., ii, 240.
McDole, G. R. See F. J. Alway.
Magli, G., ii, 237.
Magli, G. See also A. Piutti.
Magnusson, J. P., ii, 241.
Makovetzi, A., ii, 300.
Malysheff, B. V. See S. N. Antonoff.
Marchand, H. See E. Kayser.
Marchlewski, L., i, 368.
Marino, L. See A. Angeli.
Maron, D., i, 350.
Martinelli, M. See L. Mascarelli.
Mascarelli, L., and M. Martinelli, ii, 228.
Massenez, K. See F. Fischer.
Mayer, P. See C. Neuberg.
Mays, K., ii, 281.
Meisenburg, ii, 313.
Meldola, R. (Presidential Address), TRANS., 626.
Mendel, L. B. See H. G. Wells.
Menschutkin, B. N., i, 271.
Merck, E., i, 350, 356.
Merling, G., i, 315.
Merrill, G. P., and W. Tassin, ii, 278.
Metcalfe, E. P. See C. Cuthbertson.
Meth, R., i, 272.
Mettler, C., i, 315.
Meussdörffer, E. See M. Busch.
Meyer, G. M., ii, 282.
Meyer, H., i, 297, 317, 323, 342, 343.
Meyer, H., and R. Turnau, i, 344.
Meyerhofer, W., and J. H. van't Hoff, ii, 260.
Michael, A., i, 279.
Michaelis, L. See P. Rona.
Michaud, L. See O. Loeb.
Milbauer, J., ii, 252.
Millar, W. S., and W. W. Taylor, ii, 223.
Mills, J. E., ii, 226.
Miller, W. L., ii, 247.
Minet, A., ii, 250.
Mörner, C. T., ii, 283.
Moeser, L. See A. Naumann.
Mohr, L. See M. Bönninger.
Moissan, H., ii, 267.
Moodie, A. M. See J. C. Irvine.
Moore, T. S. See N. Y. Sidgwick.
Morgen, A., C. Beger, and F. Westhausser, ii, 294.
Morgenroth, J., and U. Carpi, ii, 286.
Morgenstern, F. von., ii, 293.
Moser, H. See H. Bauer.
Mossler, G., ii, 291.
Mühlinghaus, P. See W. Autenrieth.
Müller, A., ii, 272.
Müller, E. See T. Curtius.
Müller, G. See P. Friedländer.
Müller, W. See A. Naumann.
Muller, J. A., ii, 301.
Mundici, C. M. See M. Betti.
Muñoz del Castillo, J., ii, 217, 218, 219.

N.

Napper, S. S. See R. Robertson.
Naumann, A., L. Moeser, and E. Lindenbaum, ii, 273.
Naumann, A., W. Müller, and E. Lantelme, i, 314.
Neizert, C. See E. Rimbach.
Neuberg, C., and P. Mayer, i, 295.
Nierenstein, M., i, 331.
Normann, W., ii, 228.
North, H. B. See V. Lenher.
Nowak, A. See S. Zeisel.

O.

Ofner, R., ii, 310.
Olmsted, C. M., ii, 210.
Orloff, E. I., i, 365.
Osborne, T. B., and S. H. Clapp, i, 367.

P.

Packard, W. H., ii, 279.
Palazzo, F. C., and A. Tamburello, i, 298.
Paterno, E., and R. Spallino, i, 274.
Patterson, T. S., and J. Kaye, TRANS., 705.

Paul, L., i, 363.
Peirce, G. See A. S. Loevenhart.
Pellat, H., ii, 249.
Pellet, H., ii, 309.
Perotti, R., ii, 295.
Peters, L. See L. Hiltner.
Pflüger, E. See O. Hammarsten.
Phelps, I. K., and J. L. Hubbard, ii, 297.
Philip, J. C., Trans., 711.
Picard, L., ii, 318.
Pincussohn, L. See A. Bickel.
Piutti, A., i, 312.
Piutti, A., F. Cobellis, and D. Gandolfo, i, 320.
Piutti, A., and G. Magli, i, 296.
Plancher, G., and U. Ponti, i, 341.
Plato, W., ii, 239.
Plotnikoff, J., ii, 212.
Pollacci, G., ii, 289.
Pollak, J., and J. Goldstein, i, 320.
Pomeranz, C., i, 300.
Ponti, U. See G. Plancher.
Popoff, S. F., ii, 314.
Power, F. B. See M. Barrowcliff.
Pozzi-Escot, M. E., i, 355.
Pribram, R., ii, 207.
Price, T. S., Trans., 531.
Pringsheim, H., ii, 287.
Przibram, H., i, 330.
Pursel, R. C. See M. H. Webster.
Purvis, J. E., ii, 210.
Pushin, N. A., ii, 304.
Pushin, N. A. See also N. S. Kurnakoff.

R.

Raab. See F. Henrich.
Randall, D. L., ii, 303.
Rankin, G. A., ii, 254.
Ratcliff, F. D., ii, 311.
Reach, F., ii, 282.
Reichard, C., ii, 316, 319.
Reif, J. See V. Grignard.
Reychler, A., i, 275.
Rey-Pailhade, J. de, i, 372.
Richards, T. W., and G. E. Behr, ii, 222.
Richards, T. W., and F. N. Brink, ii, 258.
Richardson, F. W., ii, 297.
Riedel, J. D., i, 337.
Rimbach, E., and F. Korton, ii, 276.
Rimbach, E., and C. Neizert, ii, 269.
Robertson, R., and S. S. Napper, Trans., 761, 764.
Robertson, T. B., i, 367.
Rodie, J., ii, 306.
Rösch, J., ii, 211.
Rogowina, E. See A. Werner.
Rona, P., and L. Michaelis, i, 370.
Rosanoff, M. A., ii, 207.
Rosenfeld, L., i, 371.
Rosenheim, A., and P. Frank, ii, 271.
Rosenheim, A., and J. Hertzmann, ii, 271.
Rotarski, T. See L. Rotiniantz.
Rotiniantz, L., and T. Rotarski, ii, 226.
Rouiller, C. A. See P. A. Levene.
Rudge, W. A. D., ii, 225.
Rümelin, G., ii, 231.
Ruer, R., ii, 275.
Ruff, O., F. Eisner, and W. Heller, ii, 268.
Rupp, E., and J. Kost, ii, 298.
Ruppenthal. See F. Henrich.
Rusche, W., ii, 320.
Rutter, T. F., ii, 273.

S.

Sachs, F., and P. Alsleben, i, 356.
Salaskin, S., ii, 281.
Salkowski, E., ii, 307.
Samec, M., i, 286.
Sauton. See A. Trillat.
Schemtschuschny, S. F., ii, 258.
Scheuble, R., i, 313.
Schindelmeiser, T. See T. L. Kondakoff.
Schmidt, A., ii, 218.
Schmidt, O., i, 282, 299.
Schöndorff, B., and C. Victoroff, ii, 283.
Scholl, R., H. Berblinger, and A, Künzel, i, 354.
Scholl, R., and P. Stegmuller, i, 354.
Scholtz, M., and E. Wassermann, i, 339, 340.
Scholz, V. See H. Goldschmidt.
Schoorl, N., ii, 310.
Schreiber, H., ii, 314.
Schulze, A. See E. Fischer.
Schulze, E., ii, 293.
Schumm, O., ii, 320.
Semmler, F. W., i, 329.
Senderens, J. B., ii, 248.
Seyde, F. See H. T. Bucherer.
Sidersky, D., ii, 314.
Sidgwick, N. Y., and T. S. Moore, ii, 246.
Sidorenko, K. W., i, 270.
Sieveking, H. See C. Engler.
Simon, F., ii, 298.
Sinclair, J. E. See M. T. Bogert.
Skraup, Z. H., and K. Kaas, i, 367.
Smirnoff, W., ii, 240.

Smith, jun., W. See E. Berl.
Soddy, F., ii, 251.
Sommelet, M. See A. Béhal.
Souder, C. G. See A. Loevenhart.
Spallino, R. See E. Paterno.
Stadnikoff, G. L., i, 318.
Stefanini, A. See A. Battelli.
Stegmuller, P. See R. Scholl.
Steimmig, G. See J. Thiele.
Stevenson, R., ii, 252.
Steudel, H., i, 369.
Stoklasa, J., K. Chocenský, and A. Ernest, ii, 291.
Stolle, R., i, 359.
Stritar, M. J. See R. Fanto.
Stryzowoski, C., ii, 299.
Stscherbina, N., i, 353.
Sum, N. N. See V. E. Tistshenko.
Sustschinský, P. P., ii, 278.
Szyszkowski, B. von, ii, 238.

T.

Tamburello, A. See F. C. Palazzo.
Tanatar, S. M., ii, 261.
Tassin, W., ii, 278.
Tassin, W. See G. P. Merrill.
Taylor, W. W. See W. S. Millar.
Thiele, J., and G. Steimmig, i, 352.
Thomas, V., i, 287.
Thomas, W., ii, 311.
Thomson, J. J., ii, 220, 221.
Thorpe, J. F. See E. F. J. Atkinson.
Tichwinsky, M. M., i, 353.
Tickle, T., ii, 317.
Tiffeneau, M., i, 304.
Timmermans, J., ii, 229.
Tistshenko, V. E., A. Alexandroff, A. A. Grigoréeff, M. Gushoff, N. N. Sum, and M. N. Wischniakoff, i, 282.
Tistshenko, V. E., and G. N. Grigoréeff, i, 284.
Torrey, H. A., and H. B. Kipper, i, 325.
Traube, I., ii, 205, 207, 227.
Trechzinsky, P., i, 270.
Treitschke, W. See K. Beck.
Trillat, A., and Sauton, ii, 294.
Tsakalotos, D. E. See G. Baume.
Tschitschibabin, A. E., i, 276, 341.
Tunmann, ii, 320.
Turnau, R. See H. Meyer.

U.

Uhler, H. S. See H. C. Jones.
Ullmann, F., and J. Korselt, i, 306.
Ulrich, T., i, 331.
Underhill, F. B., ii, 285.
Uschakoff, A., i, 361.

V.

Vahlen, E., i, 331.
Vandevelde, A. J. J., i, 372.
Veraguth, H. See R. Willstätter.
Vereinigte Chininfabriken, Zimmer & Co., i, 336.
Victoroff, C. See B. Schöndorff.
Vigouroux, E., and G. Arrivaut, ii, 270.
Vitali, D., ii, 299, 302, 318.
Völker, W., ii, 311.
Voerman, G. L. See A. F. Holleman.
Voronkoff, M. P., i, 285.
Vortmann, G., 302.
Votoček, E., and J. Kastner, i, 330.

W.

Wahl, A., i, 362.
Walden, P., ii, 231.
Walter, H. See R. Wegscheider.
Walther, R. von, and H. Greifenhagen, i, 349.
Wartenberg, H. von, i, 299.
Wassermann, E. See M. Scholtz.
Wauters, J., ii, 315.
Webster, M. H., and R. C. Pursel, ii, 319.
Wedekind, E., ii, 246.
Wedekind, R., & Co., i, 327.
Wedemeyer, K., ii, 315.
Weehuizen, F., ii, 308.
Wegscheider, R., and H. Walter, ii, 259.
Weigel, O., ii, 237.
Weimann, C., i, 327.
Weimann, C. See also A. Haller.
Wells, H. G., and L. B. Mendel, ii, 282.
Wells, R. C., ii, 269.
Welsbach, C. A., von, ii, 209.
Werner, A., i, 291.
Werner, A., F. Bräunlich, C. Kreutzer, and E. Rogowina, i, 290.
Werner, A., and K. Dawe, i, 294.
Werner, E. A. See W. Caldwell.
Werner, F. See H. Ley.
Wessely, L. See S. Kohn.
Westhausser, F. See A. Morgen.
Westhausser, F., and W. Zielstorff, ii, 296.
Weyl, T., i, 305.
Wiechowski, W., ii, 283, 284.
Wiechowski, W., and H. Wiener, ii, 283.

Wiener, H. See W. Wiechowski.
Wiggin, J. D. See M. T. Bogert.
Willcock, Miss E. G., and W. B. Hardy, i, 366.
Willstätter, R., and H. Veraguth, i, 303.
Windaus, A., i, 288.
Winkelmann, A. See F. Kehrmann.
Wischniakoff, M. N. See V. E. Tistshenko.
Wolesensky, E. See V. Lenher.
Wolfes, O., i, 350.
Wood, A. See N. B. Campbell.
Wood, T. B., ii, 310.
Worms, W. W., i, 366.
Wright, R. See E. H. Farr.

Z.

Zeisel, S., and A. Nowak, ii, 276.
Zielstorff, W. See F. Westhausser.
Zincke, T., and W. Klostermann, i, 322.
Zuboff, P. W., ii, 230.
Zÿnen Wartel, H. G. F., ii, 289.
Zwicker, H. See A. Gutbier.

ERRATA.

Vol. LXXXIV (Abstr., 1903).

Part II (Index).

Page	Line	
1019	15 col. ii	*for* "A, ii, 224" *read* "A, i, 224."

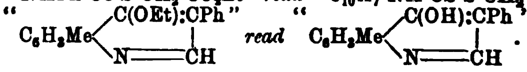
Vol. XC (Abstr., 1906).

Part I.

964	2	*for* "acetophenone" *read* "phorone."

Vol. XCII (Abstr., 1907).

Part I.

9	19*	*for* "ricin" *read* "castor oil."
9	21*	,, "cocoa butter" *read* "cocoa nut oil."
10	7	
10	8	
10	22	
105	16*	,, "benzoylconine" *read* "benzoylconiine."
105	11*	,, "conine" *read* "coniine."
113	5	,, "1881, **39**" *read* "1906, **89**."
131	17	,, "ethyl ethyl-*i*-aspartate" *read* "ethyl *i*-aspartate."
166	1*	,, "p-*hydroxyphenylazo*, &c." *read* "p-*hydroxybenzeneazo*, &c."
234	4	,, "$NHPh \cdot CS \cdot S \cdot CH_2 \cdot CO_2Et$" *read* "$C_{10}H_7 \cdot NH \cdot CS \cdot S \cdot CH_2 \cdot CO_2Et$."
242	10	,,  "$C_6H_2Me\left\langle\begin{matrix}C(OEt){:}CPh \\ N{=\!=}CH\end{matrix}\right.$" *read* "$C_6H_2Me\left\langle\begin{matrix}C(OH){:}CPh \\ N{=\!=}CH\end{matrix}\right.$".

Part II.

108	5*	*for* "lactase" *read* "lactose."
117	14	,, "Dziergowsky" *read* "Dzierzgowsky."

---

* From bottom.

of manganese from the precipitate. The colourless crystalline precipitate was then collected by the aid of the pump.

The Soluble Portion of the Oxidation Product.—The solution was made alkaline with ammonia and the precipitated oxides of manganese removed by renewed filtration. The liquid was then evaporated to dryness on the water-bath and the residue broken up before being thoroughly dried.

This was mixed with a large excess of thionyl chloride and when the violent reaction had subsided the mixture was warmed on the water-bath for half an hour. The liquid mass was then decomposed with ice and the acid chloride which separated was filtered and finally crystallised from light petroleum. The product crystallised in leaflets which melted at 68° and when examined in the polariscope gave the following figures: A chloroform solution gave α_D $+2\cdot97°$ when $c=10\cdot023$; $T=24°$; and $l=1$ dcm.; whence $[\alpha]_D$ $+30\cdot4°$.

The substance is therefore the chloride of camphor-β-sulphonic acid. Armstrong and Lowry (Trans., 1902, 81, 1447) give the melting point of this substance as 67—68° and $[\alpha]^D_{18}$ $+31\cdot1°$. Hence the soluble portion of the oxidation product is camphor-β-sulphonic acid.

The Insoluble Portion of the Oxidation Product. d-*Camphoryl-α-disulphone.*—The insoluble product of oxidation was recrystallised from hot alcohol, from which it separated in colourless prisms. These melt at 138° and are insoluble in cold water, sparingly so in cold alcohol, and readily so in chloroform, benzene, or glacial acetic acid:

0·2074 gave 0·4202 CO_2 and 0·1287 H_2O. C = 55·74; H = 6·89.

0·1689 „ 0·1892 $BaSO_4$. S = 15·38.

$C_{20}H_{30}O_6S_2$ requires C = 55·81; H = 6·97; S = 14·88 per cent.

A solution of the substance in chloroform was examined in the polariscope and α_D $+0\cdot62°$ when $c=2\cdot028$; $T=22°$; and $l=$ dcm.; hence $[\alpha]_D$ $+30\cdot6°$ and $[M]_D$ $+131\cdot6°$.

Cryoscopic determinations of the molecular weight gave the following results:

In glacial acetic acid:

0·2300 dissolved in 14·40 acetic acid gave $\Delta=0\cdot134°$; whence mol. wt. = 441.

In benzene:

0·2163 in 14·01 solvent gave $\Delta=0\cdot185°$; whence mol. wt. = 409.

$C_{20}H_{30}O_6S_2$ requires molecular weight = 430.

The crude material dissolves in a mixture of sulphuric acid and phenetole, giving a blue colour; this is no doubt due to the presence of traces of the sulphinic acid. The pure substance does not show this reaction.

Boiling water attacks camphor-α-disulphone very slowly, and after prolonged action shows a faintly acid reaction to litmus. The substance is sparingly soluble in cold alkali hydroxide, but dissolves more readily in the warm reagent, forming the alkali salts of camphorsulphonic and sulphinic acids. Thus a sample of the disulphone was warmed on the water-bath with a dilute solution of pure sodium hydroxide until all had dissolved. The solution was then acidified with dilute sulphuric acid and extracted with ether. The aqueous portion, after being neutralised, was evaporated to dryness and the residue extracted with absolute alcohol. This was filtered and the filtrate evaporated to crystallisation. The product was examined in the polariscope, and in aqueous solution the following numbers were obtained: $\alpha_D + 0{\cdot}15°$ when $c = 0{\cdot}868$; $l =$ 1 dcm.; and $T = 22°$; whence $[\alpha]_D$ $+17{\cdot}28$ and [M] (calculated for sodium camphor sulphonate) $+43{\cdot}9°$. The specific rotation of sodium *d*-camphorsulphonate was found (p. 524) to be $+18{\cdot}0°$ and $[M]_D$ $+45{\cdot}7°$.

The ethereal extract from the acidified solution was evaporated and the residue, after being purified, melted at 62—63° and gave the characteristic reaction of a sulphinic acid with phenetole and concentrated sulphuric acid.

The disulphone is also attacked by ammonia, yielding the anhydramide of camphor-β-sulphonic acid. Camphor-α-disulphone was warmed on the water-bath with strong aqueous ammonia for half an hour. The solution was then cooled and the crystalline precipitate was then collected and purified by recrystallisation from hot alcohol. It melted at 223°. A sample of camphor-β-sulphonic anhydramide prepared according to Armstrong and Lowry's method (Trans., 1902, 8, 1448) melted at the same temperature and a mixture of the substances from the two sources also showed the same melting point.

Roughly, quantitative experiments on the oxidation of the zinc sulphinate by the foregoing method showed that about 12 per cent. of the sulphinic acid is converted to sulphone and the remaining 88 per cent. to the sulphonic acid. The oxidation was also carried out in glacial acetic acid solution, when it was found that the amount converted to sulphone was rather higher, being about 18 per cent. of the original sulphinic acid. If the oxidation is carried out in alkaline solution no disulphone is formed.

Condensation of Camphor-β-sulphinic Acid with Anisole and Phenetole. Camphoryldianisylsulphonium.—Anisole was added gradually to a cold solution of zinc camporsulphinate in concentrated sulphuric acid. Immediately on adding the first portion of anisole the liquid assumed a deep blue colour, which disappeared as soon as excess of the phenolic ether was present and the whole of the sulphinic acid had been converted to the sulphonium base. After the mixture had been poured into a relatively large bulk of water the excess of anisole was removed by shaking with ether. At this stage alcohol was added to the aqueous layer to dissolve a small quantity of sulphonium sulphate which had separated as an oil. The solution was then treated with excess of barium hydroxide to remove the large excess of sulphuric acid, and the filtrate from the barium sulphate was saturated with carbon dioxide to remove barium and zinc. The carbonates of barium and zinc were then filtered and the liquid, which now contained the base as carbonate, was acidified with hydrochloric acid and precipitated with platinic chloride. In this way *camphoryldianisylsulphonium platinichloride* was obtained as a buff-coloured, insoluble precipitate. It was purified by precipitation with water from solution in acetone. After being dried in the steam oven the substance melted at 166° with profound decomposition:

0·1883 gave 0·0301 Pt. Pt = 15·99.

0·1603 „ 0·2806 CO_2 and 0·0707 H_2O. C = 47·74; H = 4·90.

$(C_{24}H_{29}O_3ClS)_2,PtCl_4$ requires C = 47·92; H = 4·83; Pt = 16·22 per cent.

The rotatory power of the substance was investigated. It was found that a solution in epichlorohydrin gave: α_D − 1·04°, when $c = 2·009$, $T = 22°$ and $l = 1$ dcm.; hence $[\alpha]_D$ − 51·8° and $[M]_D$ − 627·8°.

The *dichromate* of camphoryldianisylsulphonium was obtained as a yellow, flocculent precipitate by adding an aqueous solution of the sulphate to an acid solution of potassium chromate. The precipitate was filtered and purified by redissolving in acetone and pouring this solution into concentrated aqueous potassium dichromate. The substance, when pure, forms an orange coloured, amorphous powder which melts with decomposition at 110° and is insoluble in water, sparingly soluble in alcohol and extremely so in acetone or epichlorohydrin:

0·2460 yielded on ignition 0·0381 Cr_2O_3. Cr = 10·60.

$(C_{24}H_{29}O_3S)_2,Cr_2O_7$ requires Cr = 10·30 per cent.

Camphoryldiphenetylsulphonium.—The platinichloride of this base was obtained by a method precisely similar to that given above for the anisyl derivative.

Camphoryldiphenetylsulphonium platinichloride is a very light brown, crystalline powder which melts at 152° and is insoluble in water but very soluble in epichlorohydrin:

0·1570 gave 0·2848 CO_2 and 0·0754 H_2O. C = 49·48; H = 5·34.

0·1803 „ 0·0278 Pt. Pt = 15·42.

0·2288 „ 0·0357 Pt. Pt = 15·60.

$(C_{26}H_{33}O_3ClS)_2,PtCl_4$ requires Pt = 15·5; C = 49·60; H = 5·25 per cent.

When this substance was examined in the polariscope in epichlorohydrin solution: a_D − 1·16° when $c = 2·023$, $T = 28°$ and $l = 1$ dcm.; hence $[a]_D$ − 57·3° and $[M]_D$ − 726°.

The *dichromate* of the base forms an unstable, orange powder which melts with decomposition at 114°:

0·1892 gave 0·0277 Cr_2O_3. Cr = 10·02.

$(C_{26}H_{33}O_8S)_2,Cr_2O_7$ requires Cr = 9·76 per cent.

In conclusion, we desire to express our most hearty thanks to Professor Collie for the interest he has taken in the above experiments.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

LXXI.—The Evolution of Nitrogen Peroxide in the Decomposition of Guncotton. By **Robert Robertson**, M.A., D.Sc., and **Sidney Scrivener Napper** (*continued*) . . . 785

LXXII.—An Isomeric Change of Dehydracetic Acid. By **John Norman Collie** and **Thomas Percy Hilditch** . . . 787

LXXIII.—Measurements of the Velocities of Saponification of the *l*-Menthyl and *l*-Bornyl Esters of the Stereoisomeric Mandelic Acids. By **Alex. McKenzie** and **Herbert Bryan Thompson**, M.Sc. 789

LXXIV.—The Action of Ethyl Oxalate on Thioacetanilide and its Homologues. By **Siegfried Ruhemann** . . . 797

LXXV.—The Magnetic Rotation of Hexatriene, $CH_2\colon CH\cdot CH\colon CH\cdot CH\colon CH_2$, and its Relationship to Benzene and other Aromatic Compounds: also its Refractive Power. By **Sir William Henry Perkin** 806

LXXVI.—The Action of Tribromopropane on the Sodium Derivative of Ethyl Malonate. Part I. By **William Henry Perkin**, jun., and **John Lionel Simonsen** (Schunck Research Fellow in the University of Manchester) . . 816

LXXVII.—The Action of Tribromopropane on the Sodium Derivative of Ethyl Malonate. Part II. Formation of $\Delta^{\alpha\zeta}$-Heptadi-inene-δ-carboxylic Acid (ψ-*m*-Toluic Acid), $(CH\vdots C\cdot CH_2)_2C(CO_2H)_2$. By **William Henry Perkin**, jun., and **John Lionel Simonsen** (Schunck Research Fellow in the University of Manchester) 840

LXXVIII.—The Action of Tribromopropane on the Sodium Derivative of Ethyl Acetoacetate. By **Thomas Edward Gardner** and **William Henry Perkin**, jun. 848

PAGE

LXXIX.—Aromatic Azoimides. Part I. Parahydroxyphenylazoimide. By **Martin Onslow Forster** and **Hans Eduard Fierz** 855

LXXX.—Studies in the Camphane Series. Part XXIII. Oximes of Camphorylsemicarbazide and Camphorylazoimide. By **Martin Onslow Forster** and **Hans Eduard Fierz** . 867

LXXXI.—The Constituents of the Essential Oil of American Pennyroyal. Occurrence of a Dextro-Menthone. By **Marmaduke Barrowcliff** 875

LXXXII.—The Constitution of Homoeriodictyol.—A Crystalline Substance from Eriodictyon Leaves. By **Frederick Belding Power** and **Frank Tutin** 887

LXXXIII.—Contributions to the Chemistry of Oxygen Compounds. II. The Compounds of Cineol, Diphenylsulphoxide, Nitroso-derivatives, and the Carbamides with Acids and Salts. By **Robert Howson Pickard** and **Joseph Kenyon** 896

LXXXIV.—Freezing Point Curves of the Menthyl Mandelates. By **Alexander Findlay** and **Evelyn Marion Hickmans** . 905

LXXXV.—Acyl-ψ-derivatives of Iminothiocarbamic Acid and their Isomerides. By **Augustus Edward Dixon** and **John Taylor** 912

LXXXVI.—The Chemical Action of the Radium Emanation. Part I. Action on Distilled Water. By **Sir William Ramsay**, K.C.B., F.R.S. 931

LXXXVII.—The Chemical Changes induced in Gases submitted to the Action of Ultraviolet Light. By **David Leonard Chapman**, **Samuel Chadwick**, and **John Edwin Ramsbottom** 942

LXXXVIII.—The Velocity of Hydrolysis of the Aliphatic Amides by Alkali. By **James Codrington Crocker**, M.A., D.Sc., and **Frank Harold Lowe**, M.Sc. 952

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abati, G., i, 419.
Abati, G., and S. Minerva, i, 420.
Abderhalden, E., and B. Oppler, ii, 369.
Adler, O., ii, 378.
Alexander, P., i, 433.
Amberger, C. See C. Paal.
Ampola, G., and S. de Grazia, ii, 388.
Andreeff, I., ii, 336.
Andrlík, K., V. Staněk, and J. Urban, ii, 387.
Angeli, A., and G. Marchetti, i, 436.
Anilinfarben- und Extract-Fabriken vormals J. R. Geigy, i, 454.
Anselmino, O., i, 413.
Antonoff, G. N., ii, 334.
Argyriadès, E., ii, 393.
Aronstein, L., ii, 395.
Auclair, J., and L. Paris, ii, 381.
Auwers, K., i, 399.
Auwers, K., and M. Hessenland, i, 400.
Auwers, K., and A. Köckritz, i, 401.

B.

Backman, E. L., ii, 377.
Badische Anilin- & Soda-Fabrik, i, 407, 408, 444.
Bädeker, K., ii, 327.
Bagard, P., i, 384.
Bainbridge, F. A., and A. P. Beddard, ii, 377.
Bakunin, M., and L. Parlati, i, 415.
Balica-Iwanowska, Mme. G., ii, 386.
Barberio, M., ii, 374, 381.
Barcroft, J., and W. E. Dixon, ii, 366.
Barratt, J. O. W., i, 456.
Barrowcliff, M., TRANS., 875.
Bartal, A. von, ii, 341.
Bartelt, K. See F. W. Semmler.
Bassett, H., ii, 344.
Bates, F., and J. C. Blake, ii, 406.
Battelli, A., ii, 330.
Baumhauer, H., ii, 362.
Beckenkamp, J., ii, 362.
Beckmann, E., W. Gabel, F. Kirchhoff, O. Liesche, G. Lockemann, and E. Popa, ii, 340.
Becquerel, H., ii, 322.
Beddard, A. P. See F. A. Bainbridge.
Bedford, C. H., and R. L. Jenks, ii, 405.
Beljaeff, N. T., ii, 363.
Bellucci, I., and F. Dominici, ii, 354.
Benary, E., i, 381.
Benedict, F. G., and C. R. Manning, i, 454.
Bergell, P., i, 392, 394 ; ii, 413.
Bergtheil, C., and R. V. Briggs, ii, 415.
Berthold, E. See F. Sachs.
Bianchi, G., ii, 391.
Birckenbach, L., ii, 360.
Black, O. F. See L. J. Henderson.
Blackman, P., ii, 346.
Blaise, E. E., and M. Maire, i, 416.
Blake, J. C. See F. Bates.
Blanc, G. A., ii, 324.
Blumenfeld, E., i, 409.
Blumenthal, R. See I. Koppel.
Bodo, K. See F. W. Semmler.
Boekelman, W. A., and J. P. Staal, ii, 375.
Böeseken, J., ii, 343.
Bose, E., ii, 333.
Bose, E., and M. Bose, ii, 333.
Bose, E., and A. Müller, ii, 332.
Bose, M. See E. Bose.
Boswell, M. C., i, 407 ; ii, 411.
Bouchonnet, A., ii, 345.

Bragg, W. H., ii, 324.
Bray, W. C. See A. A. Noyes.
Bredig, G., W. Fraenkel, and E. Wilke, i, 396.
Briggs, R. V. See C. Bergtheil.
Briner, E., and E. Mettler, ii, 342.
Brissemoret, A., and R. Combes, ii, 411.
Brooks, C. See H. McGuigan.
Bruner, L., ii, 349.
Burger, A., and M. W. Neufeld, ii, 339.
Busch, M., and E. Meussdörffer, i, 448.

C.

Caldieri, S. See S. de Grazia.
Caldwell, K. S. See A. Hantzsch.
Calvi, G., and M. Malacarne, ii, 409.
Carulla, F. J. R., ii, 390.
Cassella & Co., L., i, 451.
Caudwell, B. See G. Young.
Chadwick, S. See D. L. Chapman.
Chapman, D. L., S. Chadwick, and J. E. Ramsbottom, Trans., 942.
Charitschkoff, K. W., ii, 361.
Charrier, G. See G. Ponzio.
Chauveau, A., ii, 370.
Chauvenet, E. See W. Oechsner de Coninck.
Chemische Fabrik von Heyden, i, 429.
Ciesielski, K., i, 409.
Clapp, S. H. See T. B. Osborne.
Cohn, R., ii, 409.
Coleman, C. J., ii, 367.
Collie, J. N., and T. P. Hilditch, Trans., 787.
Colson, A., ii, 356.
Comanducci, E., i, 409.
Combes, R. See A. Brissemoret.
Copaux, H., ii, 344.
Coppet, L. C. de, ii, 335.
Couchet, C., and G. Nemirowsky, ii, 345.
Cousin, H., i, 378.
Covelli, E., ii, 405.
Cramer, W. See J. Lochhead.
Criquebeuf, G. See R. Duchemin.
Crocker, J. C., and F. H. Lowe, Trans., 952.
Cuniasse, L., ii, 413.
Curtius, T., A. Darapsky, E. Müller, i, 450, 451.
Curtius, T., and E. Welde, i, 449.

D.

Dalton, J. P., ii, 330, 331, 332.
Daly, R. A., i, 407.
Darapsky, A. See T. Curtius.
Delezenne, C., ii, 369.
Derichsweiler, R., ii, 322.
Deussen, E., G. Heller, and O. Nötzel, i, 442.
Dixon, A. E., and J. Taylor, Trans., 912.
Dixon, W. E., ii, 377.
Dixon, W. E. See also J. Barcroft.
Dominici, F. See I. Bellucci.
Dormael, J. van, ii, 394.
Driessen Mareeuw, W. P. H. van den, ii, 413.
Duchemin, R., and G. Criquebeuf, ii, 409.
Durieu, ii, 374.

E.

Egeling, C. G., ii, 398.
Eggeling, H. See J. Meyer.
Ehrenpreis, A., i, 453.
Ehrlich, F., ii, 383.
Ehrström, R., ii, 370.
Elektrochemische Werke, i, 378.
Emich, F., ii, 333.
Ercolini, G. See G. Magri.
Erdmann, H., ii, 399.
Erdmann, H., and O. Makowka, ii, 399, 403.
Euler, A., and H. Euler, ii, 385.
Euler, H. See A. Euler.
Evans, C. A. L., i, 456.
Eykman, J. F., i, 378.

F.

Farbenfabriken vorm. Friedr. Bayer & Co., i, 380.
Farbwerke vorm. Meister, Lucius, & Brüning, i, 447.
Farnsteiner, K., ii, 396.
Feder, E., ii, 405.
Fetzer, K. See E. Wedekind.
Fierz, H. E. See M. O. Forster.
Fincke, H., ii, 416.
Findlay, A., and Miss E. M. Hickmans, Trans., 905.
Fischer, E., and W. A. Jacobs, i, 393.
Fischer, E., and K. Raske, i, 381.
Fischer, F., ii, 344.
Fischer, F., and H. Marx, ii, 340.
Fleckseder, R., ii, 379.
Fleig, C., ii, 372.
Fleischmann, P., and L. Michaelis, ii, 367.
Fletcher, W. M., and F. G. Hopkins, ii, 373, 409.

Foerster, F., and H. Jacoby, i, 397.
Forschbach, J., and S. Weber, ii, 378.
Forster, M. O., and H. E. Fierz, TRANS., 855, 867.
Fosse, R., i, 414.
Fouard, E., i, 391.
Frabot, C. See F. Jean.
Fraenkel, W. See G. Bredig.
Franchimont, A. P. N., i, 395.
François, M., i, 391.
Frankl, E. See R. Wegscheider.
Fribourg, C. See H. Pellet.
Friedenthal, H. See E. Salm.
Frobenius, O., and E. Hepp, i, 428.
Fröhlich, E. See E. Wedekind.
Funk, W., ii, 398.

G.

Gabel, W. See E. Beckmann.
Gallo, G., ii, 402.
Gans, R., ii, 353.
Gardner, T. E., and W. H. Perkin, jun., TRANS., 848.
Garrod, A. E., and T. S. Hele, ii, 376.
Gérard, A., i, 376.
Gibson, R. B. See L. B. Mendel.
Giran, H., ii, 329.
Girard, J. de, and A. de Saporta, ii, 400.
Glikin, J. See R. Meyer.
Grazia, S. de, and S. Caldieri, ii, 387.
Grazia, S. de. See also G. Ampola.
Greinacher, H., ii, 324.
Grignard, V., i, 398.
Grimmer, W., ii, 368.
Grosse, A. See K. Löffler.
Grunert, H. See K. Löffler.
Grunmach, L., and F. Weidert, ii, 329.
Guareschi, I., ii, 395.
Guérin, G., ii, 397.
Guild, E. J., i, 436.
Gulewitsch, W. von, i, 436.
Guye, P. A. See T. Renard.
Gyr, J., i, 416.
Gysegem, J. van, i, 375.

H.

Hahn, O., ii, 359.
Hall, G. W., ii, 369.
Haller, A., i, 377, 379.
Hallwachs, W., ii, 327.
Halpern, K. See H. Schicht.
Halphen, G., ii, 410.
Hanriot, M., ii, 386.
Hantzsch, A., and K. S. Caldwell, ii, 328.
Happel, H., ii, 331.
Hardt-Stremayr, E. R. von, i, 389, 391.
Hatai, S., ii, 371.
Hausmann, W., and W. Kolmer, ii, 380.
Heinze, B., ii, 388.
Hele, T. S. See A. E. Garrod.
Heller, G., and O. Nötzel, i, 442.
Heller, G. See also E. Deussen.
Henderson, L. J., and O. F. Black, ii, 371.
Henrard, J. T., i, 411.
Henry, L., i, 374, 377.
Hepp, E. See O. Frobenius.
Herzig, J., and R. Tscherne, i, 421.
Hessenland, M. See K. Auwers.
Hickmans, E. M. (Miss). See A. Findlay.
Hilditch, T. P. See J. N. Collie.
Hill, J. R., ii, 341.
Himstedt, F., and G. Meyer, ii, 321.
Hinterskirch, W., ii, 393.
Hoering, P., i, 411.
Hoff, J. H. van't, ii, 363.
Hoke, E., ii, 379.
Holmberg, B., i, 383.
Hopkins, F. G. See W. M. Fletcher.
Horoszkiewicz, S. von, and H. Marx, ii, 415.
Houben, J., and H. Pohl, i, 382.
Hougardy, A., ii, 374.
Huybrechts, M., ii, 397.

J.

Jacobs, W. A. See E. Fischer.
Jacoby, H. See F. Foerster.
Jaczewski, L., ii, 365.
Jänkendorf. See von Nostitz.
Javillier, M., ii, 374.
Jean, F., and C. Frabot, ii, 415.
Jenks, R. L. See C. H. Bedford.
Jenny, G. See A. Pictet.
Jodlbauer, A., i, 456.
Jordis, E., and W. Ludewig, ii, 344.
Jorissen, A., i, 434.
Jorissen, W. P., ii, 388.

K.

Kahlenberg, L., and A. S. McDaniel, ii, 326.
Karpinsky, A., ii, 362.

Kaserer, H., ii, 381.
Kayser, E., and H. Marchand, ii, 383.
Kehrmann, F., and H. Prager, i, 447.
Kempe, B., ii, 343.
Kenyon, J. See R. H. Pickard.
Kernot, G., ii, 365.
Kiliani, H., and O. Matthes, i, 382.
Kikkōji, T., i, 456.
Kirchhoff, F. See E. Beckmann.
Klein, J., i, 421.
Klever, H. W. See H. Staudinger.
Knöpfer, G., i, 423.
Knowles, G. E., ii, 389.
Köckritz, A. See K. Auwers.
Köhler, F. See E. Mohr.
Kohlrausch, F., ii, 328.
Kolmer, W. See W. Hausmann.
Konowaloff, D. P., ii, 334.
Koppel, I., and R. Blumenthal, ii, 356.
Korczynski, A. See L. Marchlewski.
Kostytscheff, S., ii, 381, 385.
Kostytscheff, S. See also W. Palladin.
Kozak, J., i, 403.
Kozniewski, P. See L. Marchlewski.
Krogh, A., ii, 366.
Krźiźan, R., ii, 390.
Kunz-Krause, H., and R. Richter, i, 419.
Kurnakoff, N. S., and G. U. Schukowsky, ii, 345.

L.

Laar, J. J. van, ii, 328.
Laue, N. J., ii, 390.
Lange, K. See R. Meyer.
Laurent, J., ii, 386.
Lazennec, I. See C. Moureu.
Leathes, J. B., ii, 376.
Ledden Hulsebosch, C. J. van, ii, 390.
Lee, F. S., ii, 373.
Leithäuser, G. See E. Warburg.
Leuchs, F., i, 408.
Leys, A., i, 379.
Liesche, O. See E. Beckmann.
Liesegang, R. E., ii, 337.
Lochhead, J., and W. Cramer, ii, 370.
Lockemann, G. See E. Beckmann.
Löffler, K., and A. Grosse, i, 439, 440.
Löffler, K., and H. Grunert, i, 441.
Löffler, K., and P. Plöcker, i, 437.
Lönnqvist, B., ii, 368.
Loewy, A., ii, 368.
London, E. S., ii, 367.
Lowe, F. H. See J. C. Crocker.
Ludewig, W. See E. Jordis.

M.

Macadie, W., ii, 410.
McDaniel, A. S. See L. Kahlenberg.
McGuigan, H., and C. Brooks, ii, 376.
Mach, F., ii, 395.
McKenzie, A., and H. B. Thompson, Trans., 789.
Maclean, H., ii, 406.
Madsen, E. H., i, 423; ii, 414.
Magri, G., and G. Ercolini, ii, 400.
Maire, M. See E. E. Blaise.
Makowka, O., ii, 403.
Makowka, O. See also H. Erdmann.
Malacarne, M. See G. Calvi.
Malengreau, F., i, 376.
Manning, C. R. See F. G. Benedict.
Manoiloff, E., ii, 380.
Marchand, H. See E. Kayser.
Marchetti, G. See A. Angeli.
Marchlewski, L., A. Korczynski, P. Kozniewski, and L. Matejko, i, 435.
Markownikoff, W. B., and V. Smirnoff, i, 418.
Martinsen, O. See R. Stoermer.
Marx, F. See C. Neuberg.
Marx, H. See F. Fischer.
Marx, H. See also S. von Horoszkiewicz.
Marx, K. See R. Meyer.
Maschmeyer, A., i, 380.
Matejko, L. See L. Marchlewski.
Mathers, F. C., ii, 352.
Matthes, O. See H. Kiliani.
Matuschek, J., ii, 349.
Meerburg, P. A., ii, 355.
Mendel, L. B., and R. B. Gibson, ii, 370.
Menschutkin, B. N., i, 386, 395.
Merck, E., i, 435, 450; ii, 349.
Merunowicz, J., and J. Zaleski, i, 455.
Mettler, E. See E. Briner.
Meussdörffer, E. See M. Busch.
Meyer, G. See F. Himstedt.
Meyer, J., and H. Eggeling, ii, 347.
Meyer, R., and J. Glikin, i, 422.
Meyer, R., and K. Lange, i, 423.
Meyer, R., and K. Marx, i, 413, 421.
Meyer, R., and H. Pfotenhauer, i, 422.
Michaelis, A., and E. Remy, i, 445.
Michaelis, L. See P. Fleischmann.
Miolck, J. See E. Rupp.
Milbauer, J., i, 388, 392.

Minerva, S. See G. Abati.
Mohr, E., and F. Köhler, i, 414.
Moissan, H., ii, 341, 360.
Morozewicz, J., ii, 396.
Moser, L., ii, 403.
Moureu, C., and I. Lazennec, i, 397.
Müller, A., ii, 376.
Müller, A. See also E. Bose.
Müller, E, See T. Curtius.
Müller, E., and F. Spitzer, ii, 351.
Muset, J., i, 374.

N.

Nardelli, G., and V. Paolini, i, 448.
Nastukoff, A. M., i, 413.
Nemirowsky, G. See C. Couchet.
Neuberg, C., i, 388.
Neuberg, C., and F. Marx, i, 387; ii, 408.
Neufeld, M. W. See A. Burger.
Niklewski, B., ii, 380.
Nötzel, O. See E. Deussen and G. Heller.
Noll, H., ii, 400.
Nostitz, von, and Jänkendorf, ii, 393.
Nowosielski, T., i, 425,
Noyes, A. A., and W. C. Bray, ii, 391.
Nozari, M., ii, 351.

O.

Oechsner de Coninck, W., ii, 353.
Oechsner de Coninck, W., and E. Chauvenet, i, 377.
Olie, jun., J., ii, 355.
Olszewski, K., ii, 331.
Oppler, B. See E. Abderhalden.
Orloff, E. I., i, 380, 382, 406.
Ornstein, G., i, 443.
Osborne, T. B., and S. H. Clapp, i, 455.

P.

Paal, C., and C. Amberger, ii, 360, 404.
Paladino, R., ii, 371.
Palladin, W., and S. Kostytscheff, ii, 385.
Paolini, V. See G. Nardelli.
Paris, L. See J. Auclair.
Parlati, L. See M. Bakunin.
Parnas, J. See R. Willstätter.
Patterson, T. S., and D. Thomson, ii, 322.
Peckolt, T., ii, 387.
Pellet, H., ii, 395, 406.
Pellet, H., and C. Fribourg, i, 388.
Perkin, Sir W. H., Trans., 806.
Perkin, W. H., jun., and J. L. Simonsen, Trans., 816, 840.
Perkin, jun., W. H. See also T. E. Gardner.
Peters, A. W., ii, 384.
Peters, W., i, 396.
Petrenko, G. J., ii, 346.
Pexsters, M., i, 376.
Pflüger, E., ii, 367.
Pfotenhauer, H. See R. Meyer.
Pfyl, B., ii, 390.
Piccinini, G., ii, 395.
Piccinini, P., ii, 378.
Pickard, R. H., and J. Kenyon, Trans., 896.
Pictet, A., and G. Jenny, i, 436.
Pictet, A., and A. Rilliet, i, 445.
Piettre, M., and A. Vila, ii, 367.
Pigorini, L., ii, 379.
Pinkus, S. N., ii, 372.
Plöcker, P. See K. Löffler.
Pohl, H. See J. Houben.
Pollacci, E., i, 397.
Pommerenke, H., ii, 392.
Ponzio, G., and G. Charrier, i, 386.
Popa, E. See E. Beckmann.
Porges, O., and E. Pribram, ii, 366.
Power, F. B., and F. Tutin, Trans., 887.
Pozzi-Escot, M. E., ii, 401, 403, 414.
Prager, H. See F. Kehrmann.
Pribram, E. See O. Porges.
Primavera, A., ii, 410.
Prior, G. T. See F. Zambonini.
Pushin, N. A., ii, 325.

R.

Raciborski, M., ii, 384, 415.
Ramsay, Sir W., Trans., 931.
Ramsbottom, J. E. See D. L. Chapman.
Raper, H. S., ii, 371.
Raske, K. See E. Fischer.
Reichard, C., ii, 391, 414.
Remy, E. See A. Michaelis.
Renard, T., and P. A. Guye, ii, 334.
Repiton, F., ii, 342, 391, 398, 409.
Richter, R. See H. Kunz-Krause.
Riegler, E., ii, 392.
Riesenfeld, E. H., and Wohlers, ii, 357.
Righi, A., ii, 324.
Rilliet, A. See A. Pictet.
Rosati, A., ii, 359.
Rothe, W., ii, 368.

Rudolfi, E., ii, 352.
Ruhemann, S., TRANS., 797.
Rupp, E., and J. Mielck, ii, 391.

S.

Sachs, F., E. Berthold, and B. Zaar, i, 426.
Salm, E., and H. Friedenthal, ii, 389.
Salomone, G., ii, 412.
Saporta, A. de. See A. de Girard.
Saposhnikoff, A. V., i, 390.
Sauton. See A. Trillat.
Schaefer, G., ii, 371.
Schicht, H., and K. Halpern, ii, 410.
Schmidt, F. W., ii, 358.
Schmidt, O., ii, 321.
Schoorl, N., ii, 388.
Schreiber, H. See P. H. Walker.
Schreinemakers, F. A. H., ii, 337.
Schukowsky, G. U. See N. S. Kurnakoff.
Schwalbe, C. G., i, 390.
Schwarz, C., ii, 372.
Schwenkenbecher, and Spitta, ii, 375.
Seaman, W. H., ii, 398.
Seifert, W., ii, 382.
Semmler, F. W., i, 433.
Semmler, F. W., and K. Bartelt, i, 429.
Semmler, F. W., and K. Bode, i, 431.
Serra, A., ii, 361.
Shukoff, I., ii, 329.
Simonsen, J. L. See W. H. Perkin, jun.
Sivén, W. O., ii, 376.
Skaupy, F., ii, 327.
Slade, J. G., ii, 379.
Smirnoff, V. I., ii, 334.
Smirnoff, V. I. See also W. B. Markownikoff.
Smirnoff, W., ii, 365.
Soddy, F., ii, 348.
Souza, D. H. de, ii, 375.
Spence, D., i, 434.
Spitalsky, E., ii, 338.
Spitta. See Schwenkenbecher.
Spitzer, F. See E. Müller.
Spriggs, E. I., ii, 377.
Spring, W., ii, 348.
Staal, J. P. See W. A. Boekelman.
Stadnikoff, G., i, 393.
Staněk, V. See K. Andrlík.
Staudinger, H., i, 424.
Staudinger, H., and H. W. Klever, i, 424.
Steiger, E., ii, 339.
Stoermer, R., and O. Martinsen, i, 446.
Stoffel, A., ii, 357.
Strandmark, J. E., ii, 364.
Struve, H., ii, 403.
Szilárd, B., ii, 357.

T.

Taylor, J. See A. E. Dixon.
Telle, H., i, 435.
Thiele, J., ii, 330.
Thiéry, ii, 408.
Thompson, H. B. See A. McKenzie.
Thomsen, J., ii, 362.
Thomson, D. See T. S. Patterson.
Tiffeneau, M., i, 404.
Traube, W., i, 396.
Trillat, A., i, 388.
Trillat, A., and Sauton, ii, 388.
Tschechowitsch, V., i, 420.
Tscherne, R. See J. Herzig.
Tschernik, G. P., ii, 362, 363.
Tschirch, A., and M. Wolff, i, 418.
Tschirwinsky, P., ii, 364.
Tschitschibabin, A. E., i, 378.
Tschugaeff, L., i, 392.
Tunmann, ii, 386.
Tutin, F. See F. B. Power.

U.

Urban, J. See K. Andrlík.
Utz, F., ii, 400.

V.

Vamvakas, J., ii, 415.
Vandevelde, A. J. J., ii, 350.
Veit, T. See E. Wedekind.
Velden, R. von der, ii, 374.
Veraguth, H. See R. Willstätter.
Vesterberg, A., ii, 390.
Vigouroux, E., ii, 354.
Vila, A. See M. Piettre.
Vorländer, D., ii, 337.
Visser, H. L., ii, 394.

W.

Walker, P. H., and H. Schreiber, ii, 397.
Wandel, ii, 380.
Warburg, E., and G. Leithäuser, ii, 342.
Watson, C., ii, 373.

Weber, S. See J. Forschbach.
Wedekind, E., K. Fetzer, and T. Veit, ii, 353.
Wedekind, E., and E. Fröhlich, i, 409, 410.
Wegscheider, R., and E. Frankl, i, 373.
Weidert, F. See L. Grunmach.
Weil, R., ii, 387.
Welde, E. See T. Curtius.
Wendt, G. von, ii, 377.
Wiechmann, F. G., ii, 407.
Wilke, E. See G. Bredig.
Willstätter, R., and J. Parnas, i, 425.
Willstätter, R., and H. Veraguth, i, 453.
Wohlers. See E. H. Riesenfeld.
Wolff, M. See A. Tschirch.

Y.

Young, G., and B. Caudwell, ii, 394.

Z.

Zaar, B. See F. Sachs.
Zaleski, J. See J. Merunowicz.
Zaleski, W., ii, 385.
Zambonini, F., and G. T. Prior, ii, 364.

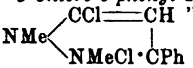
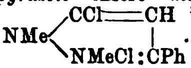
ERRATA.

Vol. XCI (Trans., 1907).

Page	Line	
335	6	*for* “ $C_{10}H_{14}O_2N_2$ ” *read* “ $C_{18}H_{14}O_2N_2$.”
350	7	,, “ $C_{35}H_{41}O_5N_5$ ” *read* “ $C_{35}H_{41}O_6N_5$.”
354	2	,, “ *αγ* ” *read* “ *αδ*.”
425	18	,, “5 : 1-Hydroxy-” *read* “1-Hydroxy-.”
548	6*	,, “ $C_2H_{10}O_2$ ” *read* “ $C_9H_{10}O_2$.”

Vol. XCII (Abstr., 1907).

Part I.

248	13*	after “ *5-Chloro-3-phenyl-1-methylpyrazole* ” insert “ *methochloride*.”
248	12*	*for* “  ” *read* “  ”.
258	20	,, “ **Sale** ” *read* “ **Salts.** ”
262	7	,, “1 : 2 : 4 : 5-tetrazine-3 : 6-carboxylic acid” *read*
262	12	“1 : 2 : 4 : 5-tetrazine-3 : 6-dicarboxylic acid.”
362	16	,; “ Wilhelm ” *read* “ Walther.”

Part II.

292	24	*for* “ $OMe\cdot C_{13}H_7(OAc)_4:NOH$ ” *read* “ $OMe\cdot C_{15}H_7(OAc)_4:NOH$.”

---

* From bottom.

No.		Decomposition.	Percentage ratio $\frac{N_2 \text{ as } NO_2}{\text{Total } N_2}$		Total N_2 in mg.	
IV.	1	Will test	42		0·67	
III.	3	In vacuum	20	21·5	0·72	0·75
III.	5	,,	23		0·77	
VII.	4	In atmosphere of CO_2	13		0·88	

The Will test is the method of decomposition which seems to be most free from complications caused by the by-products, and consequently the results given by it represent as nearly as can be obtained at present the course of the inherent decomposition of guncotton. By its means the actual or intrinsic stability of two samples may be compared, although it is not necessarily the best adapted for a practical stability test, since under ordinary conditions of storage the by-products are retained in close contact with the explosive. The presence of solid catalysts has long been considered to exercise an influence on the decomposition, and the results obtained in the present paper indicate that the gaseous products also have a measurable effect.

The presence of 40 per cent. of the total nitrogen in the form of peroxide is opposed to the results of the previous workers on this subject, but this disagreement is most probably due to their use of unsuitable apparatus and less perfect methods of estimating this gas.

Will concludes that practically the whole of the nitrogen is given off in the form of nitrogen dioxide, and gives the equation $C_{12}H_{15}(NO_2)_5O_{10} = C_{10}H_8O_8N + 4NO + 6H_2O + 2CO$ for the decomposition. This is based on the analysis of a product remaining after long-continued heating and the ratio of water (found by absorbing in a calcium chloride tube) to nitrogen in the gas evolved.

In confirmation, he quotes the observation that when the combustion tube is not sufficiently hot twice the usual volume of gas is obtained.

From Will's paper it appears that the analytical figures obtained by him do not agree with the calculated formula, $C_{10}H_8O_8N$:

Found ; $C = 44·4$; $H = 2·4$; $O = 47·9$; $N = 5·3$.
$C_{10}H_8O_8N$ requires $C = 45·3$; $H = 1·1$; $O = 48·3$; $N = 5·3$ per cent.

so that the equation is of very slight value. Moreover, the observation that the volume of gas is doubled if the combustion tube is not properly heated does not differentiate between nitrogen dioxide and peroxide, since the latter gas in these circumstances would be reduced to dioxide, the final result being the same, whatever the proportions of the two gases.

It has been previously mentioned in this paper that the volume of gas obtained when the combustion tube is omitted is less than the usual volume of nitrogen, which conclusively shows that nitrogen peroxide is present, the loss being due to absorption of dioxide and peroxide in the potash solution.

The experiment of long duration, quoted on p. 779, was carried out in a similar manner to that described by Will, and, for the period during which it was continued, confirms his result that the total quantity of nitrogen evolved per quarter hour remains constant. This was not the case with the composition of the gases, since the ratio of nitrogen as peroxide to total nitrogen, which remained at 40 to 50 per cent. for the first eighty quarter-hours (five times the period of the usual test), fell to about 10 per cent. after 260 quarter-hours, when the guncotton, originally containing 13 per cent. of nitrogen, had lost nitrogen equal to 4 per cent.

It is therefore evident that the equation proposed by Will does not represent the primary mode of decomposition of guncotton, as no account is taken of the presence of nitrogen peroxide; nor do his equation and formula agree with his analytical figures, while his observation of the double volume of gas is equally in agreement with the presence of nitrogen peroxide.

The long-continued experiments also serve to throw some further light on the results obtained by Hoitsema and Saposchnikoff, since it appears that the products of continued heating give a smaller proportion of nitrogen peroxide than is obtained by the action of heat on a pure nitrocellulose. But in the early stages of decomposition, and while the substance can still be described as a "nitrocellulose," the nitrogen is to a large extent evolved as peroxide.

The results of this research may be briefly summarised in the statement that, although previous observers have stated that only traces of nitrogen peroxide exist in the gaseous decomposition products of guncotton, it has been shown that, when due precautions are taken to exclude the action of liquid water and of the heated guncotton on the gases evolved, nearly one-half of the nitrogen evolved is present as peroxide, even when a considerable proportion of its nitrogen has already been disengaged from the guncotton molecule.

Finally, we would like to express our indebtedness to Lt.-Col. Sir Frederic Nathan for his valuable assistance and advice in connexion with this and the preceding paper.

ROYAL GUNPOWDER FACTORY,
WALTHAM ABBEY.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

LXXXIX.—Arsenic Di-iodide. By John Theodore Hewitt and Thomas Field Winmill 962

XC.—Separation of Cadmium from Zinc as Sulphide in the presence of Trichloroacetic Acid. By John Jacob Fox . 964

XCI.—Mixed Semi-ortho-oxalic Compounds. By G. Druce Lander 967

XCII.—The Influence of Substitution in the Nucleus on the Rate of Oxidation of the Side-Chain. III. The Oxidation of the Nitro- and Chloronitro-derivatives of Toluene. By Julius Berend Cohen and Henry James Hodsman 970

XCIII.—The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide. Part I. By Arthur Lapworth and Elkan Wechsler 977

XCIV.—Studies of the Perhalogen Salts. Part I. By Charles Kenneth Tinkler, B.Sc. 996

XCV.—The Formation and Reactions of Imino-compounds. Part IV. The Formation of 1 : 4-Naphthylenediamine from Ethyl γ-Imino-α-cyano-γ-phenylbutyrate. By Jocelyn Field Thorpe 1004

XCVI.—Some Compounds of Guanidine with Sugars. Part I. By Robert Selby Morrell and Albert Ernest Bellars . 1010

XCVII.—Esterification Constants of Substituted Acrylic Acids. Part II. By John Joseph Sudborough and Ebenezer Rees Thomas 1033

PAGE

XCVIII.—The Addition of Iodine to Acetylenic Acids. By THOMAS CAMPBELL JAMES and JOHN JOSEPH SUDBOROUGH . 1037

XCIX.—Mercury Derivatives of Pseudo-Acids containing the Group ·CO·NH·. By S. J. MANSON AULD, Ph.D. . . 1045

C.—The Constitution of the Diazo-compounds. By JOHN CANNELL CAIN 1049

CI.—Experimental Investigation into the Process of Dyeing. By JULIUS HÜBNER 1057

CII.—Brazilin and Hæmatoxylin. Part VII. Synthesis of Derivatives of Hydrindene closely allied to Brazilin and Hæmatoxylin. By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON 1073

CIII.—The Action of Aluminium Chloride on Naphthalene. By ANNIE HOMER, B.A., Bathurst Student at Newnham College, Cambridge 1103

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E., i, 476.
Abderhalden, E., and L. Baumann, i, 572.
Abderhalden, E., L. Baumann, and E. S. London, ii, 489.
Abderhalden, E., and H. Deetjen, ii, 486.
Abderhalden, E., and O. Emmerling, ii, 497.
Abderhalden, E., C. Funk, and E. S. London, ii, 487.
Abderhalden, E., A. Gigon, and E. Strauss, ii, 488.
Abderhalden, E., and A. H. Koelker, ii, 488.
Abderhalden, E., and H. Přibram, i, 570.
Abderhalden, E., and T. Sasaki, i, 573.
Abderhalden, E., and A. Schittenhelm, ii, 489.
Abderhalden, E. See also E. Fischer.
Ackermann, D., and F. Kutscher, ii, 491.
Ackermann, E. See P. Rabe.
Acree, S. F., i, 562.
Acree, S. F., and J. M. Johnson, i, 506.
Agostinelli, C. See R. Ciusa
Altmayer, V. See M. Mayer.
Andrews, L. W., ii, 503.
Andrlik, K., and V. Staněk, ii, 511.
Angeli, A., and G. Marchetti, i, 551.
Anschütz, R., J. Drugman, F. Haas, O. Scharfenberg, and O. Sieplein, i, 468.
Apitzsch, H., i, 537.
Auld, S. J. M., TRANS., 1045.
Austerweil, G. See E. Berl.
Austrian, C. R. See W. Jones.
Auwers, K., i, 554.

B.

Baborovský, G., and V. Vojtěch, ii, 420.
Bacon, R. F., ii, 500.
Bacon, R. F., and P. C. Freer, i, 479.
Bacon, R. F., and H. T. Marshall, ii, 497.
Badische Anilin- und Soda-Fabrik, i, 478, 507, 589.
Bagard, P., i, 476.
Bakker, G., ii, 434.
Balbiano, L., G. de Conno, and V. Paolini, i, 522.
Bamberger, E., i, 516, 517, 518, 521.
Bamberger, E., and J. Brun, i, 520.
Bamberger, E., and J. Frei, i, 519.
Bang, I., V. Bohm, and M. Ljungdahl, ii, 487.
Barbier, P., and P. Sisley, i, 563.
Barbieri, G. A., ii, 462, 466, 467.
Barbieri, G. A., and A. Volpino, ii, 465.
Bauer, H. See H. Wieland.
Baumann, L. See E. Abderhalden.
Bearn, A. R., and W. Cramer, i, 576.
Beckmann, E., and P. Danckwortt, ii, 508.
Béhal, A., and M. Sommelet, i, 460.
Behrend, R., i, 481.
Bellars, A. E. See R. S. Morrell.
Bellucci, I., and E. Clavari, ii, 474.
Bellucci, I., and F. Carnevali, ii, 472.
Benedict, F. G., A. R. Diefendorf, and V. C. Myers, ii, 492.

Benz, M. See R. Willstätter.
Berg, W. N., and W. J. Gies, i, 573.
Berkeley, Earl of, ii, 440.
Berl, E., and G. Austerweil, ii, 457.
Berl, E. See also A. Werner.
Bernoulli, A. L. See P. Nordmeyer.
Betts, A. G., and R. H. Sherry, ii, 449.
Bial, M., and O. Wandel, ii, 497.
Binet du Jassonneix, A., ii, 474.
Birnie, S., ii, 469.
Bloch, A. See T. Klobb.
Boeke, H. E., and F. Rinne, ii, 471.
Bogert, M. T., and H. A. Seil, i, 560.
Bohm, V. See I. Bang.
Bohrmann, L. See W. Steinkopf.
Bolton, W. von, ii, 478.
Borchers, E. See A. Hantzsch.
Borden, J. H., ii, 494.
Bose, E., ii, 435, 442.
Boudouard, O., and H. Le Chatelier, i, 460.
Bourquelot, E., ii, 510.
Bouveault, L., and R. Locquin, i, 479.
Bowman, F. C., ii, 456.
Bradley, C. E., ii, 499.
Bradshaw, L., ii, 450.
Bradshaw, L. See H. B. Dixon.
Braun, J. von, i, 524.
Bresler, H. W., W. H. Friedemann, and J. Mai, i, 567.
Briner, E., and E. Cardoso, ii, 436.
Brissemoret, A., ii, 515.
Brown, E. D. See T. Sollmann.
Browning, P. E., and W. A. Drushel, ii, 505.
Brun, J. See E. Bamberger.
Bruninghaus, L., ii, 419.
Bucherer, H. T., and F. Seyde, i, 509.
Bugge, G. See K. A. Hofmann.
Buglia, G., and I. Simon, ii, 485.
Burger, A., ii, 466.
Burke, W. E. See S. W. Young.
Busch, M., i, 564.
Busch, M., and R. Hobein, i, 535, 552.

C.

Cain, J. C., Trans., 1049.
Cambi, L., i, 460.
Cameron, F. K., and W. O. Robinson, ii, 444.
Campbell, E. DeMille, ii, 446.
Cardoso, E. See E. Briner.
Carnevali, F. See I. Bellucci.
Carrara, G., ii, 431.
Carson, C. M., ii, 451.
Cederberg, H. See A. Tschirch.
Chabrié, C., ii, 477.
Chace, A. F., and W. J. Gies, ii, 496.
Chapman, A. C., and P. Whitteridge, ii, 513.
Chodat, R., and J. Pasmanik, i, 575.
Chodat, R., and Staub, i, 574.
Chuit, P., and J. Demant, i, 535.
Chwala, A. See P. Friedländer.
Ciamician, G. L., and P. Silber, i, 484.
Ciusa, R., and C. Agostinelli, i, 553.
Clarke, J. W. See A. E. Garrod.
Clavari, E. See I. Bellucci.
Clover, A. M., i, 542.
Cohen, J. B., and H. J. Hodsman, Trans., 970.
Cohnheim, O., ii, 487.
Colson, A., ii, 474.
Cone, L. H., and C. S. Robinson, i, 504.
Conno, G. de. See L. Balbiano.
Cornu, F., ii, 488.
Cramer, W. See A. R. Bearn.
Crane, J. E., and C. M. Joyce, ii, 514.

D.

Dakin, H. D., ii, 490.
Danckwortt, P. See E. Beckmann.
Danjou, E., ii, 510.
D'Ans, J., ii, 458.
Daufresne. See M. Tiffeneau.
Deetjen, H. See E. Abderhalden.
Defacqz, E., ii, 475.
Delacre, M., i, 459.
Delépine, M., i, 484.
Demant, J. See P. Chuit.
Deventer, C. M. van, ii, 456.
Diefendorf, A. R. See F. G. Benedict.
Diels, O., and H. Stein, i, 528.
Diels, O., and M. Stern, i, 466, 480.
Ditz, H., ii, 459, 511.
Dixon, H. B., and L. Bradshaw, ii, 450.
Dover, M. V. See E. P. Kohler.
Drabble, E., H. Drabble, and D. G. Scott, ii, 499.
Drabble, H. See E. Drabble.
Drugman, J. See R. Anschütz.
Drushel, W. A. See P. E. Browning.
Dubois, W. L., ii, 513.
Dukelski, M., ii, 463.
Dumont, J., and C. Dupont, ii, 501.
Duparc, L., and F. Pearce, ii, 484.
Dupont, C. See J. Dumont.

E.

Eakle, A. S., ii, 484.
Ebler, E., ii, 485.
Edner, J. See A. Tschirch.
Einbeck, H. See R. Pschorr.
Eldredge, C. G., and L. M. Liddle, ii, 501.
Elster, J., and H. Geitel, ii, 423.
Emmerling, O. See E. Abderhalden.
Eucken, A., ii, 425.
Euler, H., i, 574.

F.

Fahrion, W., ii, 514.
Falke, V. See R. Schenk.
Falta, W., F. Grote, and R. Staehelin, ii, 486.
Fanto, R. See M. J. Stritar.
Farbenfabriken vorm. Friedr. Bayer & Co., i, 568.
Faust, O., ii, 426.
Fauvel, P., ii, 493.
Fernbach, A. See J. Wolff.
Fiederer, M. See R. F. Weinland.
Fischer, E., i, 485.
Fischer, E., and E. Abderhalden, ii, 487.
Fischer, E., and E. Koenigs, i, 486.
Fittig, R., P. Kraus, F. Lentz, J. von Panayeff, and W. Peters, i, 471.
Flaschner, O., ii, 454.
Foerster, F., and J. Wolf, ii, 508.
Folin, O., ii, 494, 503.
Foote, H. W., and L. H. Levy, ii, 440.
Forbes, G. S. See T. W. Richards.
Forsyth, D., ii, 491.
Fox, J. J., Trans., 964.
François, M., ii, 503.
Frazer, J. C. W. See H. N. Morse.
Freer, P. C. See R. F. Bacon.
Frei, J. See E. Bamberger.
Frese, H. See W. Schneidewind.
Friedemann, W. H. See H. W. Bresler.
Friedländer, P., A. Chwala, and Z. Slubek, i, 525.
Fröhlich, E., and E. Wedekind, i, 512.
Fuchs, K. See W. Küster.
Fühner, H., and E. Neubauer, ii, 485.
Funk, C. See E. Abderhalden.

G.

Gabutti, E., ii, 512.
Gahren, A. See D. Vorländer.
Garelli, F., ii, 465.
Garnier, C. See J. de Kowalski.
Garrod, A. E., and J. W. Clarke, ii, 495.
Gaubert, P., ii, 479.
Gautier, M. See P. A. Guye.
Gehrcke, E., and O. Reichenheim, ii, 421.
Geitel, H. See J. Elster.
Gies, W. J. See W. N. Berg.
Gies, W. J. See also A. F. Chace.
Gigon, A. See E. Abderhalden.
Glassner, F., i, 533.
Glover, W. H. See A. Hantzsch.
Godchot, M. See E. Jungfleisch.
Goldschmiedt, G., ii, 450.
Gomberg, M., i, 504.
Gooch, F. A., and H. D. Newton, ii, 507.
Gorsline, E. E. See J. B. Tingle.
Gottrau, H. de. See F. Kehrmann.
Grassi, U., ii, 425.
Greifenhagen, H. See R. von Walther.
Greinacher, H., and M. Kernbaum, ii, 422.
Grélot, P., ii, 513.
Grote, F. See W. Falta.
Grün, A., and P. Schacht, i, 462.
Grün, A., and E. Theimer, i, 464.
Guérin, G., ii, 512.
Guillet, L., ii, 461, 473.
Gustavson, G., ii, 468.
Gutt, J., i, 508.
Guttmann, L. F., i, 458; ii, 433.
Guye, P. A., ii, 437.
Guye, P. A., and M. Gautier, ii, 417.
Guyot, A. See A. Haller.

H.

Haas, F. See R. Anschütz.
Haber, F., and R. Le Rossignol, ii, 454.
Hackett, F. E. See J. A. McClelland.
Haller, A., and A. Guyot, i, 565.
Hantzsch, A., ii, 418.
Hantzsch, A., E. Borchers, E. Hedley, and A. H. Salway, i, 500.
Hantzsch, A., and W. H. Glover, i, 538.
Hantzsch, A., and H. Hibbert, i, 496.
Hantzsch, A., and K. Meisenburg, i, 513.
Hantzsch, A., and A. Salway, i, 555.
Harries, C. D., and K. Kircher, i, 466.

Harries, C. D., and K. Langheld, i, 571.
Harris, C. E. See W. G. Little.
Hasslinger, R. von, ii, 429.
Hatcher, R. A., and C. G. L. Wolf, ii, 490.
Hauser, O., ii, 470.
Hawley, L. F., ii, 460, 506.
Hedley, E. See A. Hantzsch.
Heinemann, P. G., ii, 498.
Heinze, B., ii, 502.
Henderson, P., ii, 426.
Hepner, A. See T. Pfeiffer.
Hermann, H., ii, 442.
Herzog, J., i, 512.
Hewitt, J. T., and T. F. Winmill, TRANS., 962.
Heyn, E., ii, 428.
Higley, L. A., i, 461.
Hibbert, H. See A. Hantzsch.
Hildebrandt, H., ii, 496.
Hill, A. E. See M. A. Rosonoff.
Hinrichs, G. D., ii, 450.
Hinrichsen, F. W., E. Kedesdy, V. Rodt, and F. Thomas, ii, 506.
Hirsch, A. See E. P. Schoch.
Hobein, R. See M. Busch.
Hodsman, H. J. See J. B. Cohen.
Hoebel, O., i, 557.
Hörlein, H. See L. Knorr.
Hofmann, K. A., and G. Bugge, i, 489.
Holde, D., ii, 514.
Holdermann, K. See R. Scholl.
Holland, W. W. See H. N. Morse.
Holmberg, B., i, 474, 475
Holmberg, B., and K. Mattisson, i, 475.
Holt, A., jun., ii, 450.
Homer, Miss A., TRANS., 1103.
Houben, J., and H. Pohl, i, 474.
Houdard, M., ii, 468.
Hubbard, J. L. See I. K. Phelps.
Hübner, J., TRANS., 1057.
Hutton, R. S., and J. E. Petavel, ii, 432.
Huybrechts, M., ii, 430.

I.

Inouye, K., i, 482.
Ipatieff, W., and W. Sdzitowecky, i, 457.
Isaac, E., and G. Tammann, ii, 469.

J.

Jaeger, F. M., ii, 441.
Jänecke, E., ii, 480.
Jahn, H., ii, 430, 433.
James, C., ii, 467.
James, T. C., and J. J. Sudborough, TRANS., 1037.
Jantsch, G. See A. Werner.
Joannis, A., ii, 459.
Johns, C. O. See H. L. Wheeler.
Johnsen, A., i, 541.
Johnson, J. M. See S. F. Acree.
Johnson, T. B. See H. L. Wheeler.
Jones, H. C., and W. R. Veazey, ii, 438.
Jones, W., and C. R. Austrian, i, 572.
Jorissen, W. P., and W. E. Ringer, ii, 422.
Joyce, C. M. See J. E. Crane.
Jungfleisch, E., and M. Godchot, i, 471.

K.

Kablukoff, I. A. See W. Luginin.
Kahn, M., ii, 460.
Kalmus, H. T. See R. Lorenz.
Karl, A., ii, 420.
Karsten, B. J., ii, 447.
Kedesdy, E. See F. W. Hinrichsen.
Kehrmann, F., C. Sabo, and Werner-Gresby, i, 563.
Kehrmann, F., H. de Gottrau, and G. Leemann, i, 554.
Kernbaum, M. See H. Greinacher.
Kesseler, H. See G. Schroeter.
Kinkels, E., ii, 516.
Kircher, K. See C. D. Harries.
Klages, A., i, 499.
Kleeman, R. D., ii, 423.
Klein, D. See A. T. Lincoln.
Kleine, A., ii, 446.
Klobb, T., and A. Bloch, i, 521.
Knoll & Co., i, 549.
Knorr, L., and H. Hörlein, i, 547, 548.
Koch, W., i, 573.
Koelker, A. H. See E. Abderhalden.
Koenigs, E. See E. Fischer.
Kohler, E. P., and M. V. Dover, i, 535.
Koninck, L. L. de, ii, 506.
Koritschoner, F., i, 532.
Kowalski, J. de, and C. Garnier, ii, 418.
Krassusky, K., i, 459.
Kraus, P. See R. Fittig.
Küster, W., i, 572.
Küster, W., and K. Fuchs, i, 572.
Kunckell, F., i, 537.
Kunz, M. A. See R. Scholl.

Kutscher, F. See D. Ackermann.
Kym, O., i, 560.

L.

Laar, J. J. van, ii, 431.
Laby, T. H., ii, 423.
Lander, G. D., Trans., 967.
Langheld, K. See C. D. Harries.
Lapworth, A., and E. Wechsler, Trans., 977.
Laxa, O., ii, 497.
Lazennec, I. See C. Moureu.
Lebeau, P., ii, 460, 479.
Le Blanc, M., ii, 505.
Le Chatelier, H. See O. Boudouard.
Leemann, G. See F. Kehrmann.
Léger, E., i, 545.
Lehmann, C. See M. Müller.
Lenher, V. See S. Weidman.
Lentz, F. See R. Fittig.
Leroide, J. See E. Tassilly.
Le Rossignol, R. See F. Haber.
Leroux, H., i, 538.
Leverkus, C. O. See G. Schroeter.
Levy, L. H. See H. W. Foote.
Levy, R. See A. Rosenheim.
Lewin, L., ii, 496.
Lewkowitsch, J., i, 521.
Lichty, D. M., ii, 445.
Liddle, L. M. See C. G. Eldredge.
Lincoln, A. T., and D. Klein, ii, 435.
Little, W. G., and C. E. Harris, ii, 486.
Ljungdahl, M. See I. Bang.
Locquin, R. See L. Bouveault.
Loeb, O., ii, 491.
Lombroso, U., ii, 490.
London, E. S. See E. Abderhalden.
Long, J. H., i, 570.
Lord, R. C., i, 467.
Lorenz, R., and H. T. Kalmus, ii, 430, 438.
Lottermoser, A., ii, 464.
Lovelace, B. F. See H. N. Morse.
Lovisato, D., ii, 482.
Luginin, W., and I. A. Kablukoff, ii, 437.
Lumière, A., L. Lumière, and A. Seyewetz, i, 573.
Lumière, L. See A. Lumière.
Lundén, H., ii, 443.
Lunt, J., ii, 456.
Lustig, F. See W. Prandtl.

M.

McClelland, J. A., and F. E. Hackett, ii, 420.
McIntosh, D., i, 458.
Magri, G., ii, 453.
Mai, J. See H. W. Bresler.
Makower, W., and S. Russ, ii, 421.
Mailhe, A. See P. Sabatier.
Mansfeld, J. See R. Scholl.
Marc, R., ii, 453.
Marchetti, G. See A. Angeli.
Marcusson, J., i, 466.
Marshall, H. T. See R. F. Bacon.
Mattisson, K. See B. Holmberg.
Maurenbrecher, A. D. See P. van Romburgh.
Mayer, M., and V. Altmayer, i, 457.
Mazzucchelli, A. See E. Paternò.
Meerwein, H., and G. Schröeter, i, 534.
Meisenburg, K. See A. Hantzsch.
Merrill, G. P., and W. Tassin, ii, 484.
Meunier, J., i, 460.
Meyer, D. See W. Schneidewind.
Meyer, J., i, 462.
Meyer, R. See J. Stark.
Moissan, H., ii, 459.
Moore, B., M. Nierenstein, and J. L. Todd, ii, 495.
Morrell, R. S., and A. E. Bellars, Trans., 1010.
Morse, H. N., J. C. W. Frazer, and W. W. Holland, ii, 440.
Morse, H. N., J. C. W. Frazer, and B. F. Lovelace, ii, 439.
Moureu, C., and I. Lazennec, i, 487.
Müller, E., ii, 428.
Müller, J., i, 482.
Müller, M., and C. Lehmann, ii, 491.
Mulder, A., i, 508.
Myers, V. C. See F. G. Benedict.

N.

Neubauer, E. See H. Fühner.
Newton, H. D. See F. A. Gooch.
Nicolardot, P., ii, 508.
Nierenstein, M. See B. Moore.
Nordmeyer, P., and A. L. Bernoulli, ii, 432.

O.

Oddo, B., i, 549.
Œchsner de Coninck, W., i, 532.
Olivari, E. See E. Rimini.
Orloff, N. A., ii, 476.

P.

Paal, C., and K. Zahn, i, 522.
Pacini, D., ii, 425.
Palazzo, F. C., i, 489.
Palmaer, W., ii, 424.
Panayeff, J. von. See R. Fittig.
Paolini, V. See L. Balbiano.
Pasmanik, J. C. R. Chodat.
Patein, G., i, 570.
Paternò, E., and A. Mazzucchelli, ii, 451.
Payne, G. A. See C. Revis.
Pearce, F. See L. Duparc.
Pellat, H., ii, 427, 428.
Pellet, H., and L. Pellet, ii, 501.
Pellet, L. See H. Pellet.
Perkin, W. H., jun., and R. Robinson, TRANS., 1073.
Petavel, J. E. See R. S. Hutton.
Peters, W. See R. Fittig.
Pfaff, F. W., ii, 480.
Pfeiffer, T., A. Hepner, and W. Schneider, ii, 491.
Phelps, I. K., and J. L. Hubbard, i, 467.
Pohl, H. See J. Houben.
Pons, C. See K. Sasaki.
Pozzi-Escot, M. E., ii, 516.
Prandtl, W., and F. Lustig, ii, 477.
Prandtl, W., and O. Rosenthal, ii, 476.
Přibram, H. See E. Abderhalden.
Prud'homme, M., i, 561.
Pschorr, R., and H. Einbeck, ii, 547.
Pyne, F. R., ii, 469.

R.

Rabe, P., and E. Ackermann, i, 546.
Raschig, F., ii, 455
Read, M. R., ii, 474.
Redgrove, H. S., ii, 446.
Reichenheim, O. See E. Gehrcke.
Reisch, R., ii, 499.
Rengade, E., ii, 457, 458.
Revis, C., and G. A. Payne, ii, 492.
Reychler, A., i, 476.
Richards, T. W., and G. S. Forbes, ii, 424.
Richter, O., i, 523.
Rimini, E., and F. Olivari, i, 522; ii, 436.
Ringer, W. E. See W. P. Jorissen.
Rinne, F. See H. E. Boeke.
Rinne, R., ii, 447.
Robinson, C. S. See L. H. Cone.
Robinson, R. See W. H. Perkin, jun.
Robinson, W. O. See F. K. Cameron.
Rodié, J., i, 544.
Rodt, V. See F. W. Hinrichsen.
Romburgh, P. van, and A. D. Maurenbrecher, i, 512.
Rosanoff, M. A., and A. E. Hill, ii, 503.
Rosenheim, A., and R. Levy, i, 489.
Rosenheim, O., ii, 512.
Rosenthal, O. See W. Prandtl.
Rowe, A. W., ii, 444.
Ruer, R., ii, 433.
Russ, S. See W. Makower.

S.

Sabatier, P., i, 458.
Sabatier, P., and A. Mailhe, i, 488, 490, 549.
Sabo, C. See F. Kehrmann.
Salway, A. H. See A. Hantzsch.
Sasaki, K., C. Pons, and M. Savarè, ii, 494.
Sasaki, T. See E. Abderhalden.
Sauton. See J. A. Trillat.
Savarè, M. See K. Sasaki.
Schacht, P. See A. Grün.
Schaller, W. T., ii, 480.
Scharfenberg, O. See R. Anschütz.
Scharizer, R., ii, 482
Schenck, R., ii, 429.
Schenk, R., H. Semiller, V. Falke, ii, 470.
Schittenhelm, A. See E. Abderhalden.
Schlotterbeck, F., i, 478.
Schmidt-Nielsen, S., i, 571.
Schmitz, R., ii, 494.
Schneider, W. See T. Pfeiffer.
Schneidewind, W., D. Meyer, and H. Frese, ii, 502.
Schoch, E. P., and A. Hirsch, ii, 473.
Schöndorff, B., ii, 493.
Scholl, R., K. Holdermann, M. A. Kunz, J. Mansfeld, and C. Stoll, i, 540.
Schroeter, G., i, 529, 576.
Schroeter, G., H. Kesseler, C. O. Leverkus, and F. Wülfing, i, 530.
Schroeter, G., and C. Stassen, i, 532.
Schroeter, G. See also H. Meerwein.
Schulze, H., i, 545.
Schulz, H. See A. Tschirch.
Scott, D. G. See E. Drabble.
Sdzitowecky, W. See W. Ipatieff.
Seemann, J., ii, 490.
Seil, H. A. See M. T. Bogert.
Semiller, H. See R. Schenk.

Seyewetz, A. See A. Lumière.
Seyde, F. See H. T. Bucherer.
Sherry, R. H. See A. G. Betts.
Shinn, F. L., ii, 417.
Sieplein, O. See R. Anschütz.
Silber, P. See G. L. Ciamician.
Simon, I. See G. Buglia.
Sisley, P. See P. Barbier.
Skrabal, A., ii, 448
Slubek, Z. See P. Friedländer.
Smith, G. McP., ii, 463.
Smith, G. McP., and J. R. Withrow, ii, 462.
Smith, J. H., ii, 491.
Smith, R. G., ii, 499.
Smith, R. G., ii, 498.
Smith, S. W. J., ii, 431.
Sollmann, T., and E. D. Brown, ii, 495.
Sommelet, M. See A. Béhal.
Spiegel, L., and P. Spiegel, i, 507.
Spiegel, P. See L. Spiegel.
Spiro, K., ii, 516.
Stadlinger, H. See W. Weichardt.
Staehelin, R. See W. Falta.
Staněk, V. See K. Andrlík.
Stark, J., ii, 417.
Stark, J., and R. Meyer, ii, 418.
Stassen, C. See G. Schroeter.
Staub. See R. Chodat.
Stein, H. See O. Diels.
Steinkopf, W., i, 488.
Steinkopf, W., and L. Bohrmann, i, 490
Štěrba, J., ii, 421.
Stern, M. See O. Diels.
Stewart, A. W. See N. T. M. Wilsmore.
Stoecker, M., ii, 504.
Stokes, H. N., ii, 471.
Stoll, C. See R. Scholl.
Stollé, R., i, 496.
Stone, G. C., and W. G. Waring, ii, 505.
Strauss, E. See E. Abderhalden.
Straw, A. See W. R. Whitney.
Stritar, M. J., and R. Fanto, i, 464.
Stromeyer, C. E., ii, 445.
Suais, E., i, 568.
Sudborough, J. J. See T. C. James.
Sudborough, J. J., and E. R. Thomas, Trans., 1033.
Surdo, A. Lo, ii, 445.
Sutherland, W., i, 569.

T.

Tammann, G., ii, 445.
Tammann, G. See also E. Isaac.
Tandler, R., ii, 434.
Tassilly, E., and J. Leroide, i, 515.
Tassin, W. See G. P. Merrill.
Teclu, N., ii, 446, 451, 504.
Theimer, E. See A. Grün.
Thomas, F. See F. W. Hinrichsen.
Thomas, E. R. See J. J. Sudborough.
Thoms, H., i, 545.
Thorpe, J. F., Trans., 1004.
Threlfall, R., ii, 453.
Tiffeneau, M., and Daufresne, i, 515.
Tingle, J. B., and E. E. Gorsline, i, 498.
Tinkler, C. K., Trans., 996.
Todd, J. L. See B. Moore.
Tommasina, T., ii, 427.
Tóth, J., ii, 513.
Traube, W., i, 557.
Trevor, J. E., ii, 426.
Trillat, J. A., and Sauton, ii, 492.
Tschelinzeff, W., i, 499.
Tschirch, A., and H. Cederberg, i, 545.
Tschirch, A., and J. Edner, ii, 501, 515.
Tschirch, A., and H. Schulz, i, 544.
Tschirwinsky, W., ii, 481.
Tschitschibabin, A. E., i, 503.
Twitchell, E., i, 465.

U.

Urban, G., i, 539.

V.

Veazey, W. R. See H. C. Jones.
Vigouroux, E., ii, 461.
Vintilesco, J., ii, 501.
Viola, C. M., ii, 483.
Völtz, W., ii, 490.
Vojtěch, V. See G. Baborovský.
Vollrath, F., ii, 514.
Volpino, A. See G. A. Barbieri.
Vorländer, D., ii, 442.
Vorländer, D., and A. Gahren, ii, 441.
Vries, H. J. F. de, ii, 504.

W.

Wagner, B., ii, 492.
Wahl, A., i, 493.
Walden, P., ii, 437.
Wallach, O., and H. Wienhaus, i, 541.
Walter, K., ii, 481.

Walther, R. von., and H. Greifenhagen, i, 551.
Wandel, O. See M. Bial.
Warcollier, G., ii, 499.
Waring, W. G. See G. C. Stone.
Watts, H. F., ii, 507.
Wechsler, E. See A. Lapworth.
Wedekind, E., i, 576.
Wedekind, E. See also E. Fröhlich.
Weichardt, W., and H. Stadlinger, i, 574.
Weidman, S., and V. Lenher, ii, 482.
Weinland, R. F., and M. Fiederer, i, 549.
Wendt, G., i, 542.
Wenyon, C. M., ii, 495.
Werner, A., E. Berl, G. Jantsch, and E. Zinggeler, i, 482.
Werner-Gresby. See F. Kehrmann.
Westerkamp, A., ii, 506.
Wheeler, A. S., ii, 511.
Wheeler, H. L., C. O. Johns, and T. B. Johnson, i, 559.
Whitney, W. R., and A. Straw, ii, 443.
Whitteridge, P. See A. C. Chapman.
Wieland, H., i, 492, 494.
Wieland, H., and H. Bauer, i, 491, 527.
Wienhaus, H. See O. Wallach.
Wiley, H. W., ii, 493.
Willstätter, R., and M. Benz, i, 566.
Wilsmore, N. T. M., and A. W. Stewart, i, 478.
Winmill, T. F. See J. T. Hewitt.
Withrow, J. R. See G. McP. Smith.
Wohlwill, F., ii, 495.
Wolf, C. G. L. See R. A. Hatcher.
Wolf, J. See F. Foerster.
Wolff, J., and A. Fernbach, i, 482.
Wülfing, F. See G. Schroeter.

Y.

Young, S. W., and W. E. Burke, ii, 433.

Z.

Zahn, K. See C. Paal.
Zerewitinoff, T., ii, 509.
Zinggeler, E. See A. Werner.

ERRATA.

Vol. XC (Abstr., 1907).

Part II.

Page	Line	
72	3*	*for* "euricic" *read* "erucic."
268	19	,, "**Molybdenum**" *read* "**Tungsten.**"
268	4*	,, "WO_2Cl_2" *read* "WO_2F_2."

Vol. XCI (Trans., 1907).

256	13*	*for* "$C_{16}H_{12}O_6N$" *read* "$C_{16}H_{19}O_6N$."
920	15*	,, "*aa*-carboxyphenylphenylthiocarbonate" *read* "*aa*-carboxyphenylphenylthiocarbamide."

---

* From bottom.

(*b*) Stable combination is preceded by the "activisation" of the interacting atoms or groups of atoms.

It will be noted that "depolarisation" of an atom or radicle in the sense employed above does not necessarily mean that the whole of the molecule or even of the atom becomes electrically neutral. Depolarisation need only necessarily occur between the atoms at which decomposition takes place, and, moreover, only at those parts of the atoms directly concerned in the decomposition.

This hypothesis would account satisfactorily for the difference between the two forms postulated by the Arrhenius theory. It is to be noted that if reaction takes place between several "depolarised" molecules, then the temperature-variation is expressed by:

$$\frac{d\log_e K}{d\theta} = \frac{q_1 + q_2 + \ldots}{R\theta^2} \quad . \quad . \quad (3)$$

where $q_1\ q_2 \ldots$ are the "heats of depolarisation" of the various interacting molecules.

According to this view the hydrolysis of acetamide by hydrochloric acid is represented as follows:

$$CH_3{\cdot}\overset{\circ}{C}O{\cdot}\overset{\circ}{N}H_2 + \overset{\circ}{H}{\cdot}\overset{\circ}{O}H + \overset{+}{H} + \overset{-}{Cl} = CH_3{\cdot}CO_2H + \overset{+}{N}H_4 + \overset{-}{Cl}.$$

The symbol ○ serves to indicate the atoms between which depolarisation has occurred. Reaction here takes place between the "depolarised" amide and water molecules, the action of the acid being regarded as catalytic. If the effect of alkali on the rate of hydrolysis of acetamide is also catalytic, then the value of B' should be the same for both reactions. Reference, however, to the above results and also to those previously given (*loc. cit.*) for the case of hydrolysis by acid, shows that for all the amides investigated these factors are much less for the reaction of hydrolysis by alkali. Evidently, then, there is some essential difference between the two reactions. The same feature is recorded by Arrhenius (*loc. cit.*) with reference to the action of acid and alkali on ethyl acetate. The factor B' was shown to be greater for hydrolysis by acid, and the view was taken that this is due to the formation of a compound of the neutral salt with the ester, which is in equilibrium with two kinds of active ester, so that B' has here a modified meaning. If hydrolysis by alkali takes place as a result of the direct action of the hydroxyl ions on the non-electrolyte molecule, then another explanation is possible, since in this case B' is determined by the heats of "electromeric" change of the non-electrolyte molecule and possibly of the hydroxyl ion. Thus, the hydrolysis of acetamide by alkali on this view would be represented as follows:

$$CH_3{\cdot}\overset{\circ}{C}O{\cdot}\overset{\circ}{N}H_2 + \overset{-}{O}H = CH_3{\cdot}\overset{-}{C}O_2 + NH_3$$

On the other hand, there is evidence to show that in some cases of hydrolysis by alkali the action of the hydroxyl ions is catalytic. The decomposition of sodium chloroacetate by alkali is a case in point (Senter, Trans., 1907, 91, 473).

Further work in the direction indicated is, however, necessary and, with the object of elucidating the function of the acid and alkali, it is intended to extend the investigation to other reactions of hydrolysis.

CHEMICAL DEPARTMENT,
S.W. POLYTECHNIC INSTITUTE,
CHELSEA, S.W.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

CIV.—Molecular Weight of β-Naphthol in Solution in Solid Naphthalene. By **Edgar Philip Perman** and **John Hughes Davies** 1114

CV.—Phenol *p*-Sulphoxide. By **Samuel Smiles** and **Alexander William Bain** 1118

CVI.—The Relation between Absorption Spectra and Chemical Constitution. Part VII. Pyridine and some of its Derivatives. By **Frank Baker** and **Edward Charles Cyril Baly** 1122

CVII.—Oxime Formation and Decomposition in Presence of Mineral Acids. By **Arthur Lapworth** 1133

CVIII.—Dibromoaminoazobenzene. By **John Theodore Hewitt** and **Norman Walker** 1138

CIX.—The Interaction of Methylene Chloride and the Sodium Derivative of Ethyl Malonate. By **Frank Tutin** . . 1141

CX.—The Chemical Composition of Petroleum from Borneo. By **Humphrey Owen Jones** and **Hubert Arthur Wootton**. 1146

CXI.—The Relation between the Crystalline Form and the Chemical Constitution of Simple Inorganic Substances. By **William Barlow** and **William Jackson Pope** . . . 1150

CXII.—Studies in Asymmetric Synthesis. VI. The Asymmetric Synthesis of the Optically Active Tartaric Acids. By **Alex. McKenzie** and **Henry Wren** 1215

CXIII.—Calmatambin: a New Glucoside. By **Frank Lee Pyman** 1228

PAGE

CXIV.—The Condensation of Aldehydes with Mixtures of α-Naphthol and α-Naphthylamine. Synthesis of 7-Aryl-$\begin{matrix}\alpha-\text{N}-\alpha\\ | \\ \beta-\text{CH}-\beta\end{matrix}$-dinaphthacridines. By **Alfred Senier** and **Percy Corlett Austin** 1233

CXV.—The Synthesis of Phenonaphthacridines: Trimethylphenonaphthacridines. By **Alfred Senier** and **Percy Corlett Austin** 1240

CXVI.—The Affinity Constants of Aminosulphonic Acids as Determined by the Aid of Methyl-Orange. By **Victor Herbert Veley** 1246

CXVII.—Colour and Constitution of Azo-compounds. Part I. By **John Theodore Hewitt** and **Herbert Victor Mitchell** 1251

CXVIII.—Some Properties of Radium Emanation. By **Alexander Thomas Cameron**, M.A., B.Sc., and **Sir William Ramsay**, K.C.B., F.R.S. 1266

CXIX.—Some Derivatives of 2-Phenyl-1 : 3-naphthylenediamine. Part I. By **Norman Lees** and **Jocelyn Field Thorpe** 1282

CXX.—New Derivatives of Diphenol (4′ : 4′-Dihydroxydiphenyl). By **James Moir**, D.Sc., M.A. 1305

CXXI.—A Series of Coloured Diazo-salts Derived from Benzoyl-1 : 4-naphthylenediamine. By **Gilbert T. Morgan** and **William Ord Wootton** 1311

CXXII.—The Oxidation of Hydrazines by Free Oxygen. By **Frederick Daniel Chattaway** 1323

CXXIII.—Studies in the Barbituric Acid Series. I. 1 : 3-Diphenylbarbituric Acid and some Coloured Derivatives. By **Martha Annie Whiteley** 1330

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E., and M. Kempe.
Adler, H. M., ii, 562.
Albahary, J. M., ii, 589.
Aloy, J., and Auber, ii, 557.
Alsleben, P. See F. Sachs.
Amberger, C. See C. Paal.
Andrews, L. W., and H. A. Carlton, ii, 575.
Anschütz, A. See R. J. Meyer.
Antonaz, A. See G. Rohde.
Archibald, E. H., ii, 526.
Aschan, O., i, 630.
Auber. See J. Aloy.
Auld, S. J. M. See W. R. Dunstan.
Austin, P. C. See A. Senier.
Auwers, K., i, 610.
Aymerich. See Prats Aymerich.

B.

Bain, A. W. See S. Smiles.
Baker, F., and E. C. C. Baly, TRANS., 1122.
Baly, E. C. C. See F. Baker.
Bamberger, E., and E. Reber, i, 643.
Bamberger, E., and L. Rudolf, i, 606.
Barlow, W., and W. J. Pope, TRANS., 1150.
Barraud, A., ii, 576.
Bauer, R., i, 603.
Benedicks, C., ii, 548.
Benedict, F. G., and T. B. Osborne, ii, 532.
Benedict, S. R., ii, 585.
Bennigson, F. See K. Friedrich.
Berg, W. N. See H. C. Sherman.
Berthold, E. See F. Sachs.
Béville, H. de, i, 628.
Billitzer, J., ii, 535.
Biltz, H., i, 646.
Biltz, W., ii, 574.
Bingham, E. C., ii, 536.
Bjerrum, N., ii, 554.
Blasdale, W. C., i, 630.
Bloch, B., ii, 563.
Bodroux, F., and F. Taboury, i, 583.
Bogert, M. T., and J. M. Nelson, i, 660.
Böhm, E., ii, 576.
Borchardt, L., ii, 563.
Borisch, P., ii, 587.
Borsche, W., i, 622.
Borsche, W., and W. Lange, i, 599.
Boudouard, O., ii, 551.
Boulud. See R. Lépine.
Bradley, H. C., ii, 567.
Braun, A., and J. Tscherniac, i, 624.
Breest, F. See J. Sand.
Broek, A. van den, ii, 523.
Brühl, J. W., ii, 517.
Brunck, O., ii, 582.
Bruninghaus, L., ii, 520.
Buchner, E., and R. Hoffmann, ii, 571.
Buckmaster, G. A., and J. A. Gardner, ii, 585.
Bütschli, O., ii, 544.
Burgess, W. T., ii, 578.
Burr, K. See H. Kauffmann.
Busch, H. See R. Pschorr.
Busquet, H., and V. Pachon, ii, 563.

C.

Cain, J. R. See H. N. Stokes.
Cameron, A. T., and Sir W. Ramsay, TRANS., 1266.
Carles, P., ii, 567.
Carlier, E. W., and C. L. Evans, ii, 569, 572.

Carlton H A. See L. W. Andrews.
Carpi, U See J. Morgenroth.
Caspari, F. See F. Straus.
Casperowicz, G., ii, 561.
Castellana, V., i, 646.
Charitschkoff, K. W., i, 590, 597.
Chattaway, F. D., Trans., 1323.
Chikashigé, M., ii, 548.
Ciamician, G., and P. Silber, i, 587.
Clapp, S. H. See T. B. Osborne.
Claussner, P. See A. Wohl.
Cochran, C. B., ii, 586.
Cohen, L. J., ii, 552.
Cohen, L. J. See also H. C. Sherman.
Cohn, P., and R. Plohn, i, 605.
Coops, G. H., ii, 590.

D

Dains, F. B., i, 596.
Darzens, G., i, 627.
Davies, J. H. See E. P. Perman.
Delacre, M., i, 578, 579, 581.
Delépine, M., i, 594.
Demjanoff, N. J., and M. Dojarenko, i, 592, 605.
Derome, E., ii, 542.
Deussen, E., ii, 576.
Dimroth, O., i, 653, 662.
Dimroth, O., M. Eble, and W. Gruhl, i, 664.
Dimroth, O., and S. Merzbacher, i, 659.
Dimroth, O., and W. von Schmaedel, i, 620.
Dobroserdoff, D., ii, 551.
Doeltz, F. O., and W. Mostowitsch, ii, 545.
Dojarenko, M. See N. J. Demjanoff.
Dorsch, R. See P. Wagner.
Dougherty, G. T., ii, 583.
Drabble, E., and D. G. Scott, ii, 571.
Dubois, W. L., ii, 587.
Dukelski, M., ii, 542.
Dunstan, W. R., S. J. M. Auld, and T. A. Henry, ii, 572.
Duval, H., i, 663.

E.

Eble, M. See O. Dimroth.
Ehrenstein, R. See P. Rabe.
Ehrlich, F., i, 592.
Einbeck, H. See R. Pschorr.
Ellis, H. R., i, 580.
Elster, J., and H. Geitel, ii, 521.
Epps, C. van. See E. W. Rockwood.
Evans, E. See O. Wallach.
Evans, C. L. See E. W. Carlier.

F.

Faber, P., ii, 557.
Falckenstein, K. V. von, ii, 538.
Falk, K. G., ii, 537.
Farsöe, V., ii, 583.
Fedoroff, E. S. von, ii, 539, 562.
Fersmann, A., ii, 561.
Fischer, E., ii, 566.
Fischl, L. See A. Ladenburg.
Fitzgerald, F. F., ii, 545.
Flanigen, A. L., ii, 580.
Fleischer, K. See O. Wallach.
Folin, O., ii, 588.
Fourneau, E., i, 622.
Franck, J., and R. Pohl, ii, 523.
Franzen, H., and F. Zimmermann, i, 661.
Frazer, J. C. W. See H. N. Morse.
Freimann, H. See E. Grandmougin.
Freund, M., and F. Mayer, i, 632.
Freund, W. See A. Wohl.
Freundlich, H., and G. Losev, ii, 534.
Friedrich, K., ii, 552.
Friedrich, K., and F. Bennigson, ii, 553.
Fries, K., and K. Kann, i, 613.
Fröhlich, A. See A. Werner.
Fröhlich, J., i, 632.

G.

Gabriel, S., i, 625.
Gabutti, E., ii, 587.
Gain, G., ii, 558.
Gardner, J. A. See G. A. Buckmaster.
Garrett, A. E., ii, 524.
Geitel, H. See J. Elster.
Gerum, J. See C. Paal.
Glassmann, B., ii, 545.
Glikón, W., ii, 566.
Goldberg, I., R. Maag, and M. Nimerovsky, i, 621.
Goris, i, 631.
Gossner, B., ii, 532.
Graaff, W. C. de, ii, 588.
Gramont, A. de, ii, 517.
Grandmougin, E., ii, 588.
Grandmougin, E., and H. Freimann, i, 664.
Granger, A., ii, 542.
Graumann, C. A., ii, 545.
Grossmann, H., ii, 556.
Grossmann, H., and B. Schück, ii, 582.
Grube, K., ii, 565.
Grüneberg, H. See A. Stock.
Gruhl, W. See O. Dimroth.

Guertler, W., ii, 524.
Guillet, L., ii, 551.
Gunn, A., and E. F. Harrison, ii, 591.
Guyot, A., i, 640, 641.

H.

Hall, R. D., ii, 555.
Halle, W. L. See R. Pschorr.
Hals, S. See P. Wagner.
Hamonet, J. L, i, 581.
Hardy, H., and B. E. Richens, ii, 531.
Harries, C., and H. O. Türk, i, 587.
Harrison, E. F. See A. Gunn.
Hartl, F. See L. Vanino.
Hartley, N., ii, 517.
Hébert, A., and F. Heim, ii, 569, 578.
Heim, F. See A. Hébert.
Heinze, B., ii, 572.
Henry, L., i, 587.
Henry, T. A. See W. R. Dunstan.
Hermann, H., ii, 544, 578.
Herold, V. See F. Sachs.
Hewitt, J. T., and H. V. Mitchell, Trans., 1251.
Hewitt, J. T., and N. Walker, Trans., 1138.
Hildebrand, J. H., ii, 574.
Hinard G., ii, 590.
Hinrichs, G. D., ii, 539.
Hoering, P., i, 624.
Hoffmann, F., and R. Rothe, ii, 539.
Hoffmann, R. See E. Buchner.
Hofmann, K. A., and V. Wölfl, ii, 521.
Hohorst, C. von. See T. Zincke.
Holde, D., and F. Schwarz, ii, 590.
Horn, D. W., i, 595; ii, 532.
Houdard, M., ii, 550.
Hüfner, G. von, ii, 552.
Humnicki, V., i, 655.

J.

Jackson, D. E. See S. A. Matthews.
Jentys, E., i, 589.
Job, A., ii, 553.
Jones, H. O., and H. A. Wootton, Trans., 1146.
Jorissen, W. P., and W. E. Ringer, ii, 520.

K.

Kann, K. See K. Fries.
Kauffmann, H., ii, 519.
Kauffmann, H., and K. Burr, i, 605, 609.
Kehrmann, F., and F. Wentzel, i, 601.
Kempe, M. See E. Abderhalden.
Klages, A., i, 597.
Kling, A., and P. Roy, i, 586.
Komarowsky, A., ii, 577.
Korschun, S. W., ii, 576.
Korshun, S. W. See also P. Nawiasky.
Kostytscheff, S., ii, 571.
Kowalevsky, K., and M. Markewicz, ii, 569.
Krauss, R. See C. Liebermann.
Kütscher, F., ii, 568.
Kunze, R. See P. Wagner.
Kurnakoff, N. S., and S. F. Schemtchuschny, ii, 525.
Kursanoff, N., i, 599, 600.
Kutscher, F., i, 634.
Kyes, P., ii, 569.

L.

Ladenburg, A., i, 668.
Ladenburg, A., and L. Fischl, i, 586.
Lämmel, R., ii, 530.
Lampén, A., ii, 584.
Landolf, E., ii, 567.
Lange, W. See W. Borsche.
Langness, J., ii, 585.
Langstein, L., and C. Neuberg, ii, 568.
Lapworth, A., Trans., 1133.
Lavesson, H., ii, 586.
Lebeau, P., ii, 540.
Lees, N., and J. F. Thorpe, Trans., 1282.
Léger, E., i, 631.
Lelli, F. F., ii, 578.
Lépine, R., and Boulud, ii, 562.
Lerch, F. von, ii, 522.
Lespieau, R., i, 580.
Leturc, E., ii, 589.
Levene, P. A. See J. H. Mandel.
Levin, M., ii, 522.
Leys, A., i, 582.
Lidoff, A. P., ii, 574.
Liebermann, C., and R. Krauss, i, 657.
Liesegang, R. E., ii, 533.
Lind, S. C., and B. C. Trueblood, ii, 583.
Lips, L. H. See A. Wohl.
Locquin, R., i, 593.
Loeb, J., ii, 565.
Lohmann, A., ii, 566.
London, E. S., ii, 563.
Losev, G. See H. Freundlich.
Luther, R., and T. F. Rutter, ii, 555.
Lutz, O., ii, 581.

M.

Maag, R. See F. Ullmann, and I. Goldberg.

McAdam, jun., D. J. See R. C. Wells.
MacKay, G. M. J., ii, 540.
McKenzie, A., and H. Wren, TRANS., 1215.
Magnan, A., ii, 566.
Mailhe, A. See P. Sabatier.
Mandel, J. H., and P. A. Levene, ii, 565.
Marchionesci, M., i, 634.
Markewicz, M. See K. Kowalevsky.
Markwalder, J., i, 637.
Matthes, H., and O. Rammstedt, ii, 592.
Matthews, S. A., and D. E. Jackson, ii, 569.
Matthews, S. A. See also O. Riddle.
Mayeda, M., ii, 591.
Mayer, F. See M. Freund.
Mayer, W., and B. Tollens, i, 588; ii, 586.
Mazurevitsch, I., i, 623.
Mazzucchelli, A., ii, 549.
Mendel, L. B., and F. P. Underhill, ii, 563.
Menschutkin, B. N., i, 582.
Merzbacher, S. See O. Dimroth.
Mestrezat, W., ii, 588.
Meunier, J., i, 579.
Meyer, E., ii, 521.
Meyer, H., i, 625.
Meyer, R. J., and A. Anschütz, ii, 557.
Meyer, R. J., and A. Schweitzer, ii, 581.
Michaelis, L., and P. Róna, i, 667.
Mitchell, H. V. See J. T. Hewitt.
Mitchell, P. H., ii, 565.
Moir, J., TRANS., 1305.
Moore, C. W. See R. Willstätter.
Morgan, G. T., and W. O. Wootton, TRANS., 1311.
Morgenroth, J., and U. Carpi, ii, 570.
Morozoff, N., ii, 536.
Morse, H. N., J. C. W. Frazer, and F. M. Rogers, ii, 533.
Moser, L., ii, 549.
Mostowitsch, W. See F. O. Doeltz.
Müller, E., and H. Schellhaas, ii, 539.
Müller, F. C. G., ii, 538.
Mumm, O., ii, 527, 528.
Murúa, A. See A. Schaeffer.

N.

Nacken, R., ii, 530, 546.
Nasini, R., ii, 519.
Nawiasky, P., and S. W. Korshun, ii, 579.
Nelson, J. M. See M. T. Bogert.
Neubauer, H., ii, 578.
Neuberg, C., i, 577.
Neuberg, C., and C. Reicher, ii, 570.
Neuberg, C. See also L. Langstein.
Nicolaier, A., i, 656.
Nimerovsky, M. See I. Goldberg.

O.

Oddo, B., i, 668.
Œchsner de Coninck, W., i, 621.
Offe, G., i, 645.
Orloff, N. A., ii, 549.
Osborne, T. B., and S. H. Clapp, i, 666.
Osborne, T. B. See F. G. Benedict.
Ostrogovich, A., and T. Silbermann, i, 647, 648.
Ostromisslensky, I. von, i, 596.
Otolski, S. W., i, 666.

P.

Paal, C., and C. Amberger, ii, 559.
Paal, C., and J. Gerum, ii, 559.
Pachon, V. See H. Busquet.
Padoa, M., i, 636.
Pélabon, H., ii, 547.
Pellet, H., ii, 580.
Perman, E. P., ii, 538.
Perman, E. P., and J. H. Davies, TRANS., 1114.
Plohn, R. See P. Cohn.
Plotnikoff, W. A., i, 580.
Pohl, R. See J. Franck.
Pope, W. J. See W. Barlow.
Popovici, J., i, 628.
Popp, M. See P. Wagner.
Prats Aymerich, J., ii, 543, 573.
Preti, L., i, 668.
Prud'homme, M., ii, 527.
Pschorr, R., i, 635.
Pschorr, R., and H. Busch, i, 636.
Pschorr, R., H. Einbeck, and O. Spangenberg, i, 635.
Pschorr, R., and W. L. Halle, i, 636.
Pschorr, R., and O. Spangenberg, i, 635.
Puccianti, L., ii, 533.
Pyman, F. L., TRANS., 1228.

R.

Rabe, P., and R. Ehrenstein, i, 626.
Raikow, P. N., i, 666.
Ramberg, L., i, 586, 604.
Rammstedt, O. See H. Matthes.
Ramsay, Sir W., ii, 541.
Ramsay, Sir W. See also A. T. Cameron.
Rassbach, W. See R. Schenck.

Reber, E. See E. Bamberger.
Recoura, A., ii, 552.
Reichard, C., ii, 592.
Reicher, C. See C. Neuberg.
Reitzenstein, F., and W. Schwerdt, i, 648.
Repiton, F., ii, 580.
Reverdin, F., i, 620.
Richens, B. E. See H. Hardy.
Riddle, O., and S. A. Matthews, ii, 562.
Riegler, E., ii, 575.
Ringer, W. E. See W. P. Jorissen.
Robertson, P. W., ii, 580.
Robertson, T. B., i, 666.
Rockwood, E. W., and C. van Epps, ii, 568.
Rogers, F. M. See H. N. Morse.
Rohde, G., and A. Antonaz, i, 634.
Rohland, P., ii, 519.
Róna, P. See L. Michaelis.
Rothe, R. See F. Hoffmann.
Roy, P. See A. Kling.
Rudolf, L. See E. Bamberger.
Rutter, T. F. See R. Luther.

S.

Sabatier, P., and A. Mailhe, i, 587.
Sachs, F. ii, 563.
Sachs, F., and E. Berthold, i, 651.
Sachs, F., V. Herold, and P. Alsleben, i, 628.
Sahmen, R., and A. von Vegesack, ii, 532.
Salkowski, E., i, 656.
Sand, J., and F. Breest, ii, 537.
Schaeffer, A., and A. Murúa, i, 609.
Schaeffer, H., ii, 518.
Schellack, E. See O. Wallach.
Schellhaas, H. See E. Müller.
Schemtchuschny, S. F. See N. S. Kurnakoff.
Schenck, R., and W. Rassbach, ii, 546.
Schidrowitz, P., ii, 585.
Schittenhelm, A., ii, 564.
Schmaedel, W. von. See O. Dimroth.
Schmidlin, J., i, 601.
Schmidt, G. C., ii, 523.
Schmidt, H. W., ii, 520.
Schmidt, J., and J. Söll, i, 630.
Schöndorff, B., ii, 591.
Schreyer, F. See T. Zincke.
Schroeter, G., i, 620.
Schück, B. See H. Grossmann.
Schulze, E., ii, 572.
Schwarz, F. See D. Holde.
Schweitzer, A. See R. J. Meyer.
Schwerdt, W. See F. Reitzenstein.
Scott, D. G. See E. Drabble.
Senderens, J. B., i, 577.
Senier, A., and P. C. Austin, TRANS., 1238, 1240.
Sherman, H. C., W. N. Berg, L. J. Cohen, and W. G. Whitman, ii, 568.
Silber, P. See G. Ciamician.
Silbermann, T. See A. Ostrogovich.
Simmermacher, W. See P. Wagner.
Sims, W. E., ii, 574.
Slavjanoff, A. N., i, 578.
Smiles, S., and A. W. Bain, TRANS., 1118.
Söll, J. See J. Schmidt.
Spangenberg, O. See R. Pschorr.
Speransky, N. A., i, 627.
Spezia, G., ii, 561.
Stock, A., and H. Grüneberg, ii, 541.
Stoddart, C. W. See A. R. Whitson.
Stokes, H. N., and J. R. Cain, ii, 581.
Stollé, R., i, 654.
Stören, R., ii, 582.
Straus, F., and F. Caspari, i, 609.
Sumner, F. B., ii, 567.
Svedberg, T., ii, 529, 535, 536.

T.

Taboury, F. See F. Bodroux.
Taylor, A. E., i, 665.
Teruuchi, Y., ii, 571.
Thomas, V., ii, 547.
Thorpe, J. F. See N. Lees.
Tollens, B. See W. Mayer.
Trueblood, B. C. See S. C. Lind.
Tsakalotos, D. E., ii, 531.
Tscherniac, J. See A. Braun.
Tschugaeff, L., i, 595.
Türk, H. O. See C. Harries.
Tutin, F., TRANS., 1141.

U.

Ullmann, F., and R. Maag, i, 638.
Underhill, F. P. See L. B. Mendel.
Ustjanzeff, W., ii, 564.

V.

Vanino, L., and F. Hartl, ii, 558.
Vegesack, A. von. See R. Sahmen.
Veley, V. H., TRANS., 1246.
Vigouroux, E., ii, 543.
Vitali, D., ii, 579.
Vrooman, C. H., ii, 566.

W.

Wagner, L., i, 589.
Wagner, P., R. Dorsch, S. Hals, and M. Popp, ii, 573.

Wagner, P., K. Kunze, and W. Simmermacher, ii, 577.
Walden, P., ii, 519.
Walker, N. See J. T. Hewitt.
Walker, P. M., ii, 585.
Wallach, O., i, 602.
Wallach, O., E. Evans, K. Fleischer, and E. Schellack, i, 616.
Walton, jun., J. H., ii, 584.
Wedekind, E., ii, 530.
Wells, R. C., and D. J. McAdam, jun., ii, 542.
Wentzel, F. See F. Kehrmann.
Werner, A., ii, 560.
Werner, A., and A. Fröhlich, i, 590.
Whiteley, M. A., TRANS., 1330.
Whitman, W. G. See H. C. Sherman.
Whitson, A. R., and C. W. Stoddart, ii, 573.
Willstätter, R., and C. W. Moore, i, 641.
Wilson, T. M., ii, 562.
Windaus, A., i, 610.
Witmer, L. F., ii, 584.
Wohl, A., i, 583.
Wohl, A., and P. Claussner, i, 585.
Wohl, A., and W. Freund, i, 584.
Wohl, A., and L. H. Lips, i, 583, 584.
Wohlgemuth, J., ii, 564.
Wölfl, V. See K. A. Hofmann.
Wootton, H. A. See H. O. Jones.
Wootton, W. O. See G. T. Morgan.
Worden, E. C., ii, 551.
Wren, H. See A. McKenzie.

Z.

Zimmermann, F. See H. Franzen.
Zincke, T., and C. von Hohorst, i, 614.
Zincke, T., and F. Schreyer, i, 625.

ERRATA.

COLLECTIVE INDEX, 1893—1902.

Page	Line	Col.	
1651	6	i	*for* "imino*di*thio-" *read* "iminothio-."

VOL. LXXXIV (ABSTR., 1903).

PART I.

841	13*	*for* "$\cdot CO_2Et$" *read* "$\cdot CO_2H$."

VOL. XC (ABSTR., 1906).

PART I.

145	3	*for* "1905" *read* "1906."
663	3*	,, "88°" *read* "70—71°."

VOL. XCII (ABSTR., 1907).

PART I.

224	23	*for* "**Acyl Derivatives**" *read* "**Aryl Derivatives.**"
326†	16	,, "WILHELM" *read* "WALTHER."
429	17 23	,, "$C_{10}H_7O\cdot CO\cdot$" *read* "$C_{10}H_{17}\cdot CO\cdot$"

PART II.

420 5 *et seq.* should read: "Lecoq de Boisbaudran has stated (Abstr., 1887, 3) that calcium sulphate phosphoresces green under the action of the cathode rays, and similarly the author finds that the sulphide phosphoresces yellow and the phosphate red under these conditions."

---

* From below.

† Not page 362 as given in Erratum in May No., p. ix.

results may be taken to support the formula $C_{40}H_{26}$ for the parent hydrocarbon.

(I) 1 *Molecule of* $C_{40}H_{26}$: 2 *Molecules of Bromine.*

0·1961 gave 0·5091 CO_2 and 0·0700 H_2O. C = 70·7 ; H = 4·00.
0·2198 „ 0·1280 AgBr. Br = 24·8.
$C_{40}H_{24}Br_2$ requires C = 72·3 ; H = 3·6 ; Br = 24·1 per cent.

(II) 1 *Molecule of* $C_{40}H_{26}$: 3 *Molecules of Bromine.*

0·1918 gave 0·4515 CO_2 and 0·0570 H_2O. C = 64·2 ; H = 3·33.
0·2170 „ 0·1704 AgBr. Br = 33·4.
0·1157 „ 0·0877 AgBr. Br = 32·2.
$C_{40}H_{23}Br_3$ requires C = 64·6 ; H = 3·1 ; Br = 32·3 per cent.

(III) 1 *Molecule of* $C_{40}H_{26}$: 4 *Molecules of Bromine.*

0·2023 gave 0·4368 CO_2 and 0·0647 H_2O. C = 58·88 ; H = 3·3.
0·2010 „ 0·1853 AgBr. Br = 39·2.
$C_{40}H_{22}Br_4$ requires C = 58·4 ; H = 2·7 ; Br = 38·9 per cent.

(IV) 1 *Molecule of* $C_{40}H_{26}$: 5 *Molecules of Bromine.*

0·2808 gave 0·5313 CO_2 and 0·0665 H_2O. C = 51·7 ; H = 2·65.
0·2657 „ 0·2779 AgBr. Br = 44·6.
0·2870 „ 0·3061 AgBr. Br = 45·4.
$C_{40}H_{21}Br_5$ requires C = 53·3 ; H = 2·3 ; Br = 44·4 per cent.

Summary :

(I) The hydrocarbon to which Bischoff had assigned the formula $C_{16}H_{12}$ cannot be obtained from benzene. Its formation in Dewar and Jones' and Bischoff's reactions respectively does not depend on the presence of either nickel carbonyl or methyl chloride, but is merely due to the condensing effect of aluminium chloride on naphthalene.

(II) This hydrocarbon has not the formula $C_{16}H_{12}$, but is identical with Friedel and Crafts' ββ-dinaphthyl, $C_{20}H_{14}$, formed by a process of simple condensation.

(III) The specific effect of aluminium bromide in the above, as in other Friedel and Crafts' reactions, is the same as that of aluminium chloride.

(IV) From the product of the reaction between aluminium chloride and naphthalene, besides ββ-dinaphthyl, there have also been isolated three new hydrocarbons:

(1) $C_{14}H_{16}$, a homologue of naphthalene, probably tetramethyl- or diethylnaphthalene.

(2) $C_{26}H_{22}$, a substance with interesting spectroscopic properties probably a homologue of dinaphthanthracene $C_{22}H_{14}$.

(3) $C_{40}H_{26}$, which is probably tetranaphthyl formed by a process of condensation.

In conclusion, the author wishes to thank Mr. H. O. Jones, M.A., of Clare College, Cambridge, at whose suggestion this work was begun, for unfailing interest and valuable advice during the progress of this research.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

CXXIV.—Aromatic Azoimides. Part II. Ortho- and Metahydroxyphenylazoimides. By **Martin Onslow Forster** and **Hans Eduard Fierz** 1350

CXXV.—Methyl Dicarboxyaconitate. By **Siegfried Ruhemann**. 1359

CXXVI.—The Action of Heat on α-Hydroxycarboxylic Acids. Part III. αα′-Dihydroxysebacic Acid and its Diacetyl Derivative. By **Henry Rondel Le Sueur** 1365

CXXVII.—An Improved form of Apparatus for the Rapid Estimation of Sulphates and Salts of Barium. By **William Robert Lang** and **Thos. Boles Allen** 1370

CXXVIII.—A Method for the Determination of the Equilibrium in Aqueous Solutions of Amines, Pseudo-acids and -bases, and Lactones. By **Tom Sidney Moore** 1373

CXXIX.—The "True" Ionisation Constants and the Hydration Constants of Piperidine, Ammonia, and Triethylamine. By **Tom Sidney Moore** 1379

CXXX.—The Application of Baeyer's Reduction to Benzoin and its Derivatives. By **James Colquhoun Irvine**, D.Sc., Ph.D., and **John Weir**, M.A., B.Sc., Berry Scholar in Science 1384

CXXXI.—The Influence of Mercuric Iodide on the Formation of Sulphonium Iodides. By **Thomas Percy Hilditch** and **Samuel Smiles** 1394

PAGE

CXXXII.—The Decomposition of Mercurous and Silver Hyponitrites by Heat. By **Prafulla Chandra Rây** and **Atul Chandra Gañguli** 1399

CXXXIII.—Mercurous Hyponitrite. By **Prafulla Chandra Rây** 1404

CXXXIV.—Cupric Nitrite. By **Prafulla Chandra Rây** . 1405

CXXXV.—Researches on Morphine. Part III. By **Frederic Herbert Lees** 1408

CXXXVI.—Phenylbenzometoxazone and Related Derivatives. By **Arthur Walsh Titherley** 1419

CXXXVII.—*iso*Nitroso- and Nitro-dimethyldihydroresorcin. By **Paul Haas** 1433

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E. See E. Fischer.
Abel, E., ii, 601.
Achelis, W., and F. Kutscher, ii, 638.
Acree, S. F., ii, 659.
Adan, R., ii, 651, 657.
Aickelin, H. See A. von Baeyor.
Allard, E., ii, 639.
Allen, T. B. See W. R. Lang.
Allison, A., ii, 654.
Amerio, A., ii, 593.
Antonoff, G. N., ii, 606.
Arndt, K., ii, 598.
Arndt, K., and K. Willner, ii, 599.
Aron, H., ii, 652.
Arzibacheff, B. See N. D. Zelinsky.
Astruc, A. See E. Baud.

B.

Baer, J., and L. Blum, ii, 640.
Baeyer, A. von, and H. Aickelin, i, 691.
Bakker, G., ii, 606.
Bang, I., V. Bohm, and M. Ljungdahl, ii, 634.
Bartelt, K. See F. W. Semmler.
Baubigny, H., ii, 652.
Baud, E., and A. Astruc, ii, 605.
Bauer, A. See F. W. Hinrichsen.
Baumhauer, H., i, 689.
Bechhold, H., ii, 641.
Beckmann, H., ii, 655.
Beebe, S. P., ii, 641.
Bell, J. M., ii, 607.
Bell, J. M. See also F. K. Cameron.
Bernhart, K. See W. Koenigs
Bernoulli, W. See F. Fichter.
Bewad, I., i, 671.
Beyerinck, M. W., ii, 642.
Bianchi, G., ii, 653.
Bischoff, C. A., i, 675.
Bischoff, C. A., Differt, E. Fröhlich, and F. Ulmann, i, 697.
Bischoff, C. A., E. Fröhlich, and H. Hoffmann, i, 696.
Bjerrum, N., ii, 622, 623.
Blanc, H. G., i, 710.
Blank, P. See E. Fischer.
Blanksma, J. J. See W. A. van Ekenstein.
Blum, L. See J. Baer.
Bohm, V. See I. Bang.
Bolland, A., ii, 660.
Braun, J. von, i, 728.
Briot, A., ii, 644.
Bruylants, P., ii, 656.
Buckmaster, G. A., ii, 660.
Buckmaster, G. A. See also J. A. Gardner.
Buckney, F., i, 722.
Bütschli, O., ii, 616.
Burian, R., i, 734, 735.
Buswell, H. L. F. See B. Collingwood.

C.

Cameron, F. K., and J. M. Bell, ii, 617.
Cameron, F. K., J. M. Bell, and W. O. Robinson, ii, 648.
Camiola, G. See S. de Grazia.
Campbell, N., ii, 597.
Carles, P., ii, 655.
Carletti, O., ii, 656.
Carlson, A. J., ii, 636.
Cathcart, E. P., ii, 633.
Chatin, A. See A. Desmoulières.
Clark, R. H., ii, 609.
Cohen, N. H., i, 715.
Collingwood, B., and H. L. F. Buswell, ii, 639.

Colonna, E. See C. Montemartini.
Contardi, A. See G. Körner.
Cook, F. C., and T. C. Trescot, ii, 659.
Coppenrath, E. See J. König.
Cram, M. P. See J. B. Tingle.
Cramer, W. See A. C. Lochhead.
Crompton, H., ii, 607.
Cserhati, A., ii, 645.

D.

Dam, W. van, ii, 649.
Darapsky, A., i, 729.
Daufresne. See M. Tiffeneau.
Dejust, H. L., ii, 614.
Delange, R., i, 700.
Densch, ii, 645.
Desmoulières, A., and A. Chatin, ii, 640.
Differt. See C. A. Bischoff.
Dinner, F. See F. Reverdin.
Doeltz, F. O., and C. A. Graumann, ii, 619.
Doeltz, F. O., and W. Mostowitsch, ii, 619
Doroschewsky, A. G., and A. Rakowsky, i, 678.
Drawe, P., ii, 613.
Durham, F. M., i, 715.

E.

Eisner, F. See O. Ruff.
Ekenstein, W. A. van, and J. J. Blanksma, ii, 638.
Ellinger, A., and C. Flamand, i, 737.
Emmett, A. D., and W. J. Gies, i, 739.
Ernest, A. See J. Stoklasa,

F.

Fabris, U. See M. Padoa.
Faubel, O., ii, 635
Fichter, F., and W. Bernoulli, i, 690
Fierz, H. C. See M. O. Forster.
Finch, F. F. See J. S. Macdonald.
Fischer, A., ii, 654.
Fischer, E., and E. Abderhalden, i, 737.
Fischer, E., P. Blank, A. H. Koelker, J. Schenkel, and W. Schrauth, i, 684.
Flamand, C. See A. Ellinger.
Fleischer, J., and H. Frank, ii, 655.
Forcrand, R. de, ii, 615.
Forster, M. O., and H. E. Fierz, TRANS., 1350.
Forsyth, D., ii, 635.
Fouard, E., i, 677.
Fourneau, E., i, 740.
Frank, H. See J. Fleischer.
Frary, F. C., ii, 649.
Fredenhagen, C., ii, 593, 594.
Frevert, H. L. See T. W. Richards.
Friedrich, K., and A. Leroux, ii, 620.
Fröhlich, E. See C. A. Bischoff.
Fromm, E., and H. Höller, i, 710.
Fromm, E., and P. Schmoldt, i, 702.
Führer, H., ii, 631.

G.

Gain, G., ii, 627.
Gañguli, A. C. See P. C. Rây.
Gardner, J. A., and G. A. Buckmaster, i, 738.
Gasparini, O., ii, 650.
Gaudechon, H., ii, 621.
Giaconi, J. See M. Kohn.
Gibson, J. A. See C. R. Sanger.
Gies, W. J. See A. D. Emmett.
Giesel, F., ii, 597.
Gillett, H. W. See J. A. Wilkinson.
Glahn, W. See T. Zincke.
Glassmann, B., i, 695.
Glauser, R. T., ii, 614.
Goldschmidt, M., i, 673
Gottlieb, R., and R. Stangassinger, ii, 637.
Grau, A., and F. Russ, ii, 601.
Graumann, C. A. See F. O. Doeltz.
Grazia, S. de, and G. Camiola, ii, 641.
Greenwood, M. See L. E. Hill.
Grignard, V., and G. Vignon, i, 689.
Grimmer, W., ii, 658.
Gröger, M., ii, 624.
Guild, F. N., ii, 629.
Guillet, L., ii, 608.
Gutmann, A., i, 671.
Gutt, J. See N. D. Zelinsky.
Guye, P. A., ii, 605.

H.

Haas, P., TRANS., 1433.
Haber, F., and W. Maitland, ii, 598.
Hantzsch, A., ii, 612.
Harries, C., and A. Himmelmann, i, 714.
Hasenbaümer, J. See J. König.
Hauser, O., ii, 626.
Hausmann, J. See R. Zalozieck
Heen, P. de. See H. Micheels.
Heermann, P., ii, 625.
Henderson, L. J. See T. W. Richards.
Henderson, Y., ii, 636.

Henry, L., i, 670, 674, 677.
Herz, W., and B. Mylius, i, 671.
Hess, E. See H. Reitter.
Heyl, F. W. See T. B. Johnson.
Hildebrandt, H., i, 715.
Hilditch, T. P., and S. Smiles, TRANS., 1394.
Hill, J. R., i, 692.
Hill, L. E., and M. Greenwood, ii, 631.
Hillmann, O. See A. Michaelis.
Himmelmann, A. See C. Harries.
Hinrichs, G. D., ii, 622.
Hinrichsen, F. W., and A. Bauer, ii, 650.
Höller, H. See E. Fromm.
Hoffmann, H. See C. A. Bischoff.
Holland, P., ii, 654.
Homer, Miss A., i, 692.
Horowitz, L. M., ii, 635.
Houdard, M., ii, 621.
Hübner, O. See E. Vongerichten.

I.

Ibele, J. See W. Koenigs.
Inglis, J. K. H., ii, 613.
Irvine, J. C., and J. Weir, TRANS., 1384.

J.

Jelineck, J. See J. Stoklasa.
Job, A., i, 673.
Jodlbauer, A., ii, 595.
Jörgensen, G., ii, 652.
Johnson, T. B., and F. W. Heyl, i, 728.
Jones, H. O. See T. B. Wood.

K.

Kampschulte, W. See W. Manchot.
Karczag, L. See W. Marckwald.
Kayser, G. See A. Kötz.
Kaznelson, H., ii, 633.
Kempe, A. See A. Kötz.
Kiliani, H., i, 715.
Kiliani, H., P. Loeffler, and O. Matthes, i, 676.
Kirpal, A., i, 722.
Klopstock, H. See A. Michaelis.
Knecht, E., ii, 654.
Koch, A., and G. Lüken, ii, 647.
Koch, W., ii, 659.
Koelker, A. H. See E. Fischer.
König, J., E. Coppenrath, and J. Hasenbaümer, ii, 647.
Koenigs, W., K. Bernhart, and J. Ibele, i, 717.
Körner, G., and A. Contardi, i, 690.
Kötz, A., G. Kayser, A. Kempe, and J. Sielisch, i, 705.
Kohlrausch, F., ii, 600.
Kohn, M., i, 679, 693.
Kohn, M., and J. Giaconi, i, 680.
Kohn, M., and O. Morgenstern, i, 681, 683.
Kohn, M., and K. Schlegl, i, 682.
Kondakoff, I., i, 713.
Kondakoff, I., and I. Schindelmeiser, i, 712.
Konowaloff, D. P., ii, 602.
Kowalevsky, K. See S. Salaskin.
Kremann, R., ii. 611.
Kühl, H., ii, 627.
Kühl, H. See also R. F. Weinland.
Küttner, S., ii, 660.
Kusnetzoff, M. I., i, 669.
Kutscher, F. See W. Achelis.

L.

Lacroix, A., ii, 628.
Lang, W. R., and T. B. Allen, TRANS., 1370.
Lawaczeck, P. See J. Tafel.
Lazennec, I. See C. Moureu.
Lebeau, P., ii, 613.
Le Blanc, M. See W. Niiranen.
Lees, F. H., TRANS., 1408.
Leroux, A. See K. Friedrich
Le Sueur, H. R., TRANS., 1365.
Levy, L. A., i, 689.
Lewin, M. See P. Petrenko-Kritschenko.
Ley, H., and F. Müller, i, 730.
Lidoff, A. P., ii, 650.
Lillie, R. S., ii, 607.
Lippich, F., ii, 638.
Ljungdahl, M. See I. Bang.
Lochhead, A. C., and W. Cramer, i, 672.
Loeffler, P. See H. Kiliani.
Loew, O., ii, 644.
Losanitsch, S. M., i, 693.
Lucius, R., i. 678.
Ludwig, A., i, 702.
Lüken, G. See A. Koch.
Luther, R., ii, 610.

M.

Macdonald, J. S., and F. F. Finch, ii, 637.
Mackenzie, A. S., ii, 596.
McGuigan, H. See A. P. Mathews.
Maitland, W. See F. Haber.
Manchot, W., and W. Kampschulte, ii, 616.
Marchlewski, L., and S. Mostowski, i, 738.
Marckwald, W., and L. Karczag, i, 690.

Marcusson, J., i, 674.
Martinand, V., ii, 644.
Martinsen, H., ii, 609.
Marum, A., ii, 640.
Mascarelli, L., ii, 602.
Mathews, A. P., and H. McGuigan, ii, 636.
Matthes, O. See H. Kiliani.
Mauguin, C. See L. J. Simon.
Mayer, P., ii, 631.
Mellanby, J., ii, 631.
Mendel, L. B., ii, 634.
Mentschikowsky, F. See P. Petrenko-Kritschenko.
Meyer, E., ii, 596.
Michaelis, A., and O. Hillmann, i, 726.
Michaelis, A., and H. Klopstock, i, 735.
Michaelis, A., O. Rademacher, and E. Schmiedekampf, ii, 731.
Micheels, H., and P. de Heen, ii, 643.
Millosevich, F., ii, 628.
Moffatt, M. R., and H. S. Spiro, ii, 653.
Mohr, E., i, 721.
Montemartini, C., and E. Colonna, ii, 619.
Moore, T. S., Trans., 1373, 1379.
Morgenstern, O. See M. Kohn.
Moseshvili, J. P., ii, 606.
Mostowitsch, W. See F. O. Doeltz.
Mostowski, S. See L. Marchlewski.
Moureu, C., and I. Lazennec, i, 746.
Mueller, E. See T. W. Richards.
Müller, F. See H. Ley.
Müller, M., ii, 645.
Mylius, B. See W. Herz.

N.

Nacken, R., ii, 611.
Nasini, R., ii, 612.
Nüranen, W., and M. Le Blanc, ii, 614.

O.

Œchsner de Coninck, W., and Raynaud, ii, 613.
Oesterle, O. A., ii, 644.
Oppenheimer, C., ii, 633.
Ortoleva, G., i, 729.
Oshima, K., ii, 644.

P.

Padoa, M., and U. Fabris, i, 722.
Pauly, H., i, 709.
Pellet, H., and R. Roche, ii, 649.
Peroni, B., ii, 658.
Petrenko-Kritschenko, P., M. Lewin, and F. Mentschikowsky, i, 708.
Pfeiffer, S. See H. Rupe.
Pflüger, E., ii, 639.
Piettre, M., and A. Vila, i, 738.
Pincussohn, L., ii, 635.
Pirani, M. von, ii, 598.
Pond, R. H., ii, 641.
Pool, J. F. A., ii, 643.
Pozzi-Escot, M. E., ii, 653.
Pushin, N. A., ii, 618.

R.

Rademacher, O. See A. Michaelis.
Rakowsky, A. See A. G. Doroschewsky.
Rassbach, W. See R. Schenck.
Rây, T. P., Trans., 1404, 1405.
Rây, T. P., and A. C. Gañguli, Trans., 1399.
Raynaud. See W. Œchsner de Coninck.
Redgrove, H. S., ii, 604.
Reichard, C., ii, 658.
Reitter, H., and E. Hess, i, 677.
Reverdin, F., and F. Dinner, i, 695.
Richards, T. W., ii, 612.
Richards, T. W., H. L. Frevert, and L. J. Henderson, ii, 604.
Richards, T. W., and E. Mueller, ii, 615.
Robinson, W. O. See F. K. Cameron.
Roche, R., ii, 643.
Roche, R. See also H. Pellet.
Rohloff, C., and Shinjo, ii, 611.
Ronchèse, A., ii, 651.
Rorive, F., and B. Tollens, i, 709.
Rosenheim, A., i, 688.
Rosenheim, O., ii, 637.
Rosenstiehl, A., ii, 610.
Rosenthaler, L., ii, 605.
Rozenblat, H., ii, 633.
Rudolfi, E., i, 688.
Ruff, O., and F. Eisner, ii, 624.
Ruhemann, S., Trans., 1359 ; i, 691.
Rupe, H., S. Pfeiffer, and J. Splittgerber, i, 711.
Russ, F. See A. Gran.
Russell, A. E., ii, 640.

S.

Sadikoff, W. S., i, 740.
Salaskin, S., and K. Kowalevsky, ii, 641.
Sanger, C. R., and J. A. Gibson, ii, 654.
Schall, R. See J. Schmidt.
Schenck, R., and W. Rassbach, ii, 619.

Schenkel, J. See E. Fischer.
Schermbeck, A. J. van, ii, 648.
Schindelmeiser, I. See I. Kondakoff.
Schlegl, K. See M. Kohn.
Schlesinger, N. See N. D. Zelinsky.
Schloesser, W., ii, 649.
Schlotterbeck, F., i. 676.
Schmidt, J., and R. Schall, i, 724.
Schmiedekampf, E. See A. Michaelis.
Schmoldt, P. See E. Fromm.
Schrauth, W. See E. Fischer.
Schüler, A., i, 700.
Schüler, A. See also H. Thoms.
Schulze, E., i, 672.
Schumann, T. See R. F. Weinland.
Schwedoff, D. See N. D. Zelinsky.
Seal, C. See G. Urbain.
Seemann, J., i, 739
Seissl, J., ii, 643
Self, P. A. W., ii, 657.
Semmler, F. W., i, 714
Semmler, F. W., and K. Bartelt, i, 703
Shaffer, P. A. See C. G. L. Wolf.
Shinjo. See C. Rohloff.
Sielisch, J. See A. Kötz.
Simon, L. J., and C. Mauguin, i, 725.
Skraup, Z. H., i, 739.
Smiles, S. See T. P. Hilditch.
Smirnoff, W. P., ii, 630
Smith, C. McP., ii, 615.
Snowdon, R. C., ii, 617.
Sollmann, T., and W. W. Williams, ii, 637.
Spiro, H. S. See M. R. Moffatt.
Splittgerber, J. See H. Rupe.
Stähler, A., ii, 655.
Stangassinger, R. See R. Gottlieb.
Starkenstein, E., ii, 640.
Steinmetz, H., i, 673.
Steudel, H., i, 738.
Stock, A., and F. Wrede, ii, 604.
Stoklasa, J., J. Jelineck, and A. Ernest, ii, 642.
Storz, L. See R. F. Weinland.
Strohmer, F., ii, 646.
Stümmer, R., i, 723.
Stutzer, A., ii, 645, 646.
Süchting, H., ii, 646.
Sutherland, W., ii, 599.
Swarts, F., i, 669; ii, 612.

T.

Tafel, J., and O. Wassmuth, i, 719.
Tafel, J., and P. Lawaczeck, i, 720.
Thiel, A., and A. Windelschmidt, ii, 601.
Thoms, H., and A. Schüler, i, 696.
Tiffeneau, M., and Daufresne, i, 701.
Tingle, J. B., and M. P. Cram, i, 692.
Titherley, A. W., TRANS., 1419.
Toborffy, Z., ii, 629.
Tollens, B. See F. Rorive.
Trescot, T. C. See F. C. Cook.
Tschitschibabin, A. E., i, 691.
Twort, F. W., ii, 643.

U.

Ulmann, F. See C. A. Bischoff.
Urbain, G., and C. Seal, ii, 594.

V.

Vageler, P., ii, 646.
Vandevelde, A. J. J., ii, 609, 632.
Vignon, G. See V. Grignard.
Vigouroux, E., ii, 622.
Vila, A. See M. Piettre.
Visser, H. L., ii, 657.
Voelcker, J. A., ii, 647.
Vongerichten, E., and O. Hübner, i, 718.
Vriens, J. G. C., ii, 651.

W.

Wacker, L., i, 726.
Wallerant, F., ii, 607.
Wassmuth, O. See J. Tafel.
Wedekind, E., ii, 626.
Weibull, M., ii, 649.
Weidman, S., ii, 630.
Weinland, E., ii, 638.
Weinland, R. F., and H. Kühl, ii, 625, 626.
Weinland, R. F., and T. Schumann, ii, 623.
Weinland, R. F., and L. Storz, i, 721.
Weir, J. See J. C. Irvine.
Weiss, F., ii, 638.
Whitlock, H. P., ii, 629.
Wilkinson, J. A., and H. W. Gillett, ii, 598.
Williams, W. W. See T. Sollmann.
Willner, K. See K. Arndt.
Windelschmidt, A. See A. Thiel.
Wogau, M. von., ii, 606.
Wolf, C. G. L., ii, 634.

Wolf, C. G. L., and P. A. Shaffer, ii, 639.
Wolff, J., i, 676.
Wolter, L., ii, 652.
Wood, R. W., ii, 595.
Wood, T. B., and H. O. Jones, ii, 620.
Wrede, F. See A. Stock.

Y.

Yorke, W., i, 740.

Z.

Zaloziecki, R., and J. Hausmann, i, 674.
Zelinsky, N. D., and B. Arzibacheff, i, 691.
Zelinsky, N. D., and J. Gutt, i, 676, 709.
Zelinsky, N., and N. Schlesinger, i, 704, 720.
Zelinsky, N. D., and D. Schwedoff, i, 704.
Zincke, T., and W. Glahn, i, 698.

ERRATUM.

VOL. XCII (ABSTR., 1907).

PART II.

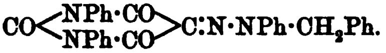
Page	Line	
520	20	*for* "1,254" *read* "1 : 254."

chloroform, benzene, or nitrobenzene, forming deep red solutions, from which, however, the yellow needles separate on evaporation.

The yellow crystals, when ground in an agate mortar, give rise to an orange-red powder, and when pressed on a smooth surface produce a bright red streak; these facts, taken in conjunction with the change of colour in solution, seem to justify the conclusion that the labile form of this compound is red, but so far it has not been obtained free from the stable yellow form. It may be mentioned, however, that on one occasion when a small quantity of the hydrazone was being prepared, a mixture of yellow needles and red prisms separated from the solution; the prisms became yellow at 200°, and melted and decomposed at 252°:

0·2875 gave 31·3 c.c. moist nitrogen at 24° and 759·3 mm. N = 12·19.
$C_{23}H_{20}O_3N_4$ requires N = 12·17 per cent.

1 : 3-*Diphenylalloxanphenylbenzylhydrazone*,



$$CO<\begin{matrix}NPh\cdot CO\\NPh\cdot CO\end{matrix}>C\!:\!N\cdot NPh\cdot CH_2Ph.$$

—Some difficulty was experienced in effecting the condensation of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid and *as*-phenylbenzylhydrazine hydrochloride. When acetic acid solutions of the two substances were mixed, a very vigorous action occurred, and a pungent tear-exciting vapour was produced, but the only compound isolated from the mixture was 1 : 3-diphenylalloxanphenylhydrazone, which melted and decomposed at 264° [0·2535 gave 32 c.c. moist nitrogen at 23·5° and 768·1 mm. N = 14·35 (theory requires N = 14·4 per cent.)].

It was found, however, that by adding phenylbenzylhydrazine hydrochloride (1 mol.) to a warm methyl-alcoholic solution of 5 : 5-dibromo-1 : 3-diphenylbarbituric acid (1 mol.), the reaction proceeded normally, the colour changing to a deep red and the solution becoming very hot. The hydrazone thus obtained formed brilliant red prisms which melted and decomposed at 130°. The yield amounted only to 50 per cent. of the calculated quantity.

1 : 3-*Diphenylalloxanphenylbenzylhydrazone* is insoluble in ether, light petroleum, or carbon tetrachloride, but dissolves readily in all the other ordinary organic solvents, forming deep red solutions from which, except in the case of benzene and toluene, the *labile* form of the hydrazone is deposited as red prisms. The red benzene solution becomes yellow on cooling and rapidly deposits the *stable* form of the hydrazone as bright yellow needles which become red at 120°, melt and decompose at 130°, and when dissolved in methyl alcohol form a red solution from which the red prisms of the *labile* form separate on

evaporation. From a toluene solution, on the other hand, a mixture of the red prisms and yellow needles is obtained:

0·2213 gave 23 c.c. moist nitrogen at 22·75° and 768·6 mm. N = 11·85.
0·1418 in 18·85 benzene gave a depression 0·089°. M.W. = 448.
$C_{29}H_{22}O_8N_4$ requires N = 11·81 per cent. M.W. = 474.

Royal College of Science, London,
South Kensington, S.W.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

CXXXVIII.—The Action of Hydrogen Peroxide on Potassium Cyanide. By **Orme Masson**, D.Sc., F.R.S. 1449

CXXXIX.—The Diazotisation of Dinitroanisidines and Related Compounds. By **Raphael Meldola**, F.R.S., and **James Gordon Hay** 1474

CXL.—Permanganic Acid. By **Matthew Moncrieff Pattison Muir** 1485

CXLI.—The Structure of Carbonium Salts. By **Frank Baker** . 1490

CXLII.—A New Colouring Matter from Nyctanthes Arbortristis. By **Ernest George Hill** and **Annoda Prasad Sirkar** 1501

CXLIII.—The Diazo-derivatives of Benzenesulphonylbenzidine. By **Gilbert T. Morgan** and **James Morton Hird** . . . 1505

CXLIV.—The Interactions of Aromatic Amines and para-Diazoimides. By **Gilbert T. Morgan** and **Frances M. G. Micklethwait** 1512

CXLV.—Succinic Acid and its Potassium Salts. By **Hugh Marshall** and **Alexander Thomas Cameron** 1519

CXLVI.—The Relation between Absorption Spectra and Optical Rotatory Power. Part II. The Tartaric Acids. By **Alfred Walter Stewart**, D.Sc. (Carnegie Research Fellow) 1537

CXLVII.—The Wandering of Bromine in the Chlorination of Bromoanilines. By **Walter William Reed** and **Kennedy Joseph Previté Orton** 1543

PAGE

CXLVIII.—Isomeric Change in Benzene Derivatives. Replacement of Halogen by Hydroxyl in Chlorobromodiazobenzenes. By KENNEDY JOSEPH PREVITÉ ORTON and WALTER WILLIAM REED. 1554

CXLIX.—The Relation between Absorption Spectra and Chemical Constitution. Part VIII. The Phenylhydrazones and Osazones of α-Diketones. By EDWARD CHARLES CYRIL BALY, WILLIAM BRADSHAW TUCK, EFFIE GWENDOLINE MARSDEN, and (in part) MAUD GAZDAR 1572

CL.—The Fluoresceins and Eosins from 4-Hydroxyphthalic, 4-Methoxyphthalic, and Hemipinic Acids. By ARTHUR FRIEDL, CHARLES WEIZMANN, and MAX WYLER 1584

CLI.—Derivatives of Naphthacenequinone. Part II. By WILLIAM HENRY BENTLEY, ARTHUR FRIEDL, and CHARLES WEIZMANN 1588

CLII.—The Chemical Action of Radium Emanation. Part II. On Solutions Containing Copper, and Lead, and on Water. By ALEXANDER THOMAS CAMERON, M.A., B.Sc., and SIR WILLIAM RAMSAY, K.C.B., F.R.S. 1593

CLIII.—Molecular Aggregation in Solution as Exemplified in Aqueous Mixtures of Sulphuric Acid with Inorganic Sulphates. By JOHN HOLMES and PHILIP JOHN SAGEMAN . 1606

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E., and **M. Kempe,** i, 808.
Abderhalden, E., and **L. Michaelis,** ii, 677.
Abderhalden, E., and **A. Voitinovici,** i, 805, 807.
Acree, S. F., and **F. Laist,** i, 796.
Albahary, J. M., ii, 715.
Alsberg, C. L. See **P. A. Levene.**
Ameseder, F., i, 745.
Amoss, H. L. See **J. H. Kastle.**
Anschütz, R., C. Hahn, and **P. Walter,** i, 766.
Arbusoff, A. E., i, 749.
Armstrong, E. F. See **H. E. Armstrong.**
Armstrong, H. E., and **E. F. Armstrong,** i, 809.
Arpi, R. See **C. Benedicks.**
Austin, A. E., ii, 711.
Austrian, C. R. See **W. Jones.**

B.

Bach, A., i, 810.
Baeyer, A. von, A. von Bentheim, and **C. Diehl,** i, 757.
Bailey, J. R., and **L. Knox,** i, 801.
Baker, F., Trans., 1490.
Baly, E. C. C., M. Gazdar, E. G. Marsden, and **W. B. Tuck,** Trans., 1572.
Barbier, P., i, 779.
Barbieri, N. A., ii, 708.
Barthe, L., i, 792.
Baudisch, O. See **F. Breinl.**
Beatty, W. A. See **P. A. Levene.**
Belonowski, G., ii, 712.
Benedicks, C., and **R. Arpi,** ii, 666.
Benrath, A., ii, 694.
Benson, C. C., ii, 709.
Bentheim, A. von. See **A. von Baeyer.**
Bentley, W. H., A. Friedl, and **C. Weizmann,** Trans., 1588.
Bergholz, R. See **A. Scheunert.**
Bernhart, C. See **W. Koenigs.**
Bertheim, A. See **P. Ehrlich.**
Berthelot, D., ii, 668, 680.
Bertrand, G., and **W. Mutermilch,** i, 811; ii, 716.
Betti, M., ii, 661.
Bevan, E. J. See **C. F. Cross.**
Bewad, I., i, 752.
Binet du Jassonneix, A., ii, 691, 692.
Bingham, E. C., ii, 669.
Bischoff, C., i, 773, 774.
Blaise, E. E., and **M. Maire,** i, 749.
Blake, G. S., and **G. F. H. Smith,** ii, 702.
Blanc, G., i, 763.
Blasdale, W. C. See **G. D. Louderback.**
Blasi, A. See **L. Mascarelli.**
Bloemendal, W. H., ii, 723.
Bodroux, F., and **F. Taboury,** i, 754.
Boes, J., i, 765.
Bondi, S., i, 766.
Borel, H. See **F. Kaufler.**
Bourion, F., ii, 690.
Bourquelot, E., and **H. Hérissey,** i, 784.
Bowman, H. L., ii, 703.
Bräuer, E. See **F. Kaufler.**
Brand, K., i, 800.
Brand, K., and **H. Zöller,** i, 755.
Brauner, B., and **B. Kuzma,** ii, 690, 716.
Breinl, F., and **O. Baudisch,** i, 807.
Briggs, J. F. See **C. F. Cross.**
Broglie, M. de, ii, 664.

Brown, M. J. See A. W. Browne.
Browne, A. W., and M. J. Brown, ii, 678, 679.
Browning, P. E., and H. E. Palmer, ii, 724.
Brunetti, W. See F. Sachs.
Burger, O. See K. A. Hofmann.

C.

Caldwell, R. J., and S. L. Courtauld, i, 809.
Cameron, A. T., and Sir W. Ramsay, TRANS., 1593.
Cameron, A. T. See H. Marshall.
Caspari, W., and H. Winternitz, ii, 708.
Castoro, N., ii, 684.
Cesaris, P., i, 780.
Chabrié, C., ii, 666.
Chapman, A. C., ii, 718.
Chapman, A. C., and H. D. Law, ii, 696.
Charabot, E., and G. Laloue, ii, 714.
Chazel, A., i, 793.
Chéneveau, C., ii, 662.
Cingolani, M. See E. Paterno.
Clapp, S. H. See T. B. Osborne.
Coehn, A., ii, 683.
Colomba, L., ii, 705.
Courtauld, S. L. See R. J. Caldwell.
Cross, C. F., E. J. Bevan, and J. F. Briggs, i, 750.

D.

Damoiseau, P. See P. Lebeau.
Davis, W. A., ii, 686.
Defacqz, E., ii, 696.
Demolon, A. See E. Kayser.
Dennstedt, M., ii, 719.
Diehl, C. See A. von Baeyer.
Dietz, W., ii, 677.
Dionneau, R., i, 747.
Doeltz, F. O., and C. A. Graumann, ii, 687, 689.
Dorner, G., ii, 709.
Ducelliez, F., ii, 693.

E.

Ehrlich, P., and A. Bertheim, i, 812.
Euler, H., i, 808.

F.

Farrington, O. C., ii, 706.
Favrel, G., i, 796.
Faworsky, A., E. Fritzmann, L. Kutscheroff, N. Sokownin, W. Tolstopjatoff, and Žinewsky, i, 741.
Fermor, L. L., ii, 700.
Fernbach, A., and J. Wolff, i, 750.
Fichter, F., ii, 691.
Filippi, F. de, ii, 707.
Flatow, L. See O. Neubauer.
Forbes, G. S. See T. W. Richards.
Forcrand, R. de, ii, 683.
Fosse, R., i, 764.
Fourneau, E., i, 762.
Fowler, G. J., and P. Gaunt, ii, 683.
Friedl, A., C. Weizmann, and M. Wyler, TRANS., 1584.
Friedl, A. See W. H. Bentley.
Friedrich, K., ii, 687.
Fritzmann, E. See A. Faworsky.
Frouin, A. See M. Nicolle.
Fuld, E., i, 807.

G.

Gagarine, Prince G., ii, 704.
Garrey, W. E., ii, 706.
Gaudechon, H., ii, 667.
Gault, H., i, 752.
Gaunt, P. See G. J. Fowler.
Gautrelet, J., and H. Gravellat, ii, 711.
Gazdar, M. See E. C. C. Baly.
Gies, W. J. See J. Rosenbloom.
Gillièron, E. See L. Pelet.
Godchot, M. See E. Jungfleisch.
Gollücke, F. See H. Stobbe.
Gooch, F. A., and F. H. Heath, ii, 720.
Gore, H. C., ii, 715.
Graham, J. C., ii, 668.
Graumann, C. A. See F. O. Doeltz.
Gravellat, H. See J. Gautrelet.
Guichard, M., ii, 689.
Guinchant, J., ii, 667.

H.

Haensel, H., i, 781.
Hahl, H. See J. Tafel.
Hahn, C. See R. Anschütz.
Hahn, O., ii, 664.
Harrington, B. J., ii, 701.
Harris, I. F. See T. B. Osborne.
Hauser, O., ii, 704.
Hay, J. G. See R. Meldola.
Heath, F. H. See F. A. Gooch.

Heller, G., and O. Nötzel, i, 800.
Henderson, L. J., and C. T. Ryder, ii, 666.
Henry, L., i, 744, 745.
Hérissey, H., and C. Lefebvre, ii, 715.
Hérissey, H. See E. Bourquelot.
Herrmann, F., ii, 689.
Herter, C. A., ii, 710.
Herwerden, M. van, i, 810.
Hesse, O., i, 777.
Hill, E. G., and A. P. Sirkar, TRANS., 1501.
Hinrichs, G. D., ii, 679.
Hird, J. M. See G. T. Morgan.
Hocheder, F. See R. Willstätter.
Hörlein, H. See L. Knorr.
Hoff, J. H. van't, ii, 702.
Hofmann, K. A., and O. Burger, i, 751.
Holmes, J., and P. J. Sageman, TRANS., 1606.
Horne, W. D., ii, 721.
Hubert, A., ii, 720.

I.

Ibele, J. See W. Koenigs.
Isaac, Miss F. See H. A. Miers.

J.

Jacobsen, A., and G. Landesen, ii, 718.
Jacoby, M., i, 811.
Jänecke, E., ii, 666, 702.
Jones, G. See T. W. Richards.
Jones, W., and C. R. Austrian, ii, 708.
Jungfleisch, E., and M. Godchot, i, 748.
Jungfleisch, E., and H. Leroux, i, 783.

K.

Kailan, A., ii, 674, 675, 676.
Kanitz, A., i, 764.
Karrer, U. See F. Kaufler.
Kastle, J. H., ii, 708.
Kastle, J. H., and H. L. Amoss, ii, 716.
Kaufler, F., i, 794.
Kaufler, F., and H. Borel, i, 794.
Kaufler, F., and E. Bräuer, i, 799.
Kaufler, F., and U. Karrer, i, 795.
Kaufler, F., and O. Thien, i, 776.
Kayser, E., and A. Demolon, ii, 714.
Keding, W. See H. Stobbe.
Kempe, M. See E. Abderhalden.
Knoop, F., i, 788.
Knorr, L., and H. Hörlein, i, 789.
Knorr, L., and P. Roth, i, 790.
Knox, L. See J. R. Bailey.
Koenigs, W., C. Bernhart, and J. Ibele, i, 791.
Kollock, L. G., and E. F. Smith, ii, 719.
Kuhn, O., ii, 678.
Kutscher, F., ii, 708.
Kutscheroff, L. See A. Faworsky.
Kuzma, B. See B. Brauner.

L.

Labrouste. See A. Leduc.
Lacroix, A., ii, 703.
Laist, F. See S. F. Acree.
Laloue, G. See E. Charabot.
Lambert, A., and C. G. L. Wolf, ii, 711.
Lampel, H., i, 804.
Lancien, A., ii, 697.
Landesen, G. See A. Jacobsen.
Law, E. F., ii, 692.
Law, H. D. See A. C. Chapman.
Lebeau, P., ii, 679.
Lebeau, P., and P. Damoiseau, ii, 680.
Leduc, A., and Labrouste, ii, 684.
Lefebvre, C. See H. Hérissey.
Leroux, H. See E. Jungfleisch.
Lesser, E. J., ii, 707.
Leuchs, H., and W. Manasse, i, 770.
Levene, P. A., i, 788; ii, 711.
Levene, P. A., and C. L. Alsberg, i, 805.
Levene, P. A., and W. A. Beatty, i, 803, 804.
Levene, P. A. See also J. A. Mandel.
Leys, A., ii, 722.
Liebermann, H., ii, 709.
Lippmann, G., ii, 668.
Lorenz, R., ii, 665.
Louderback, G. D., and W. C. Blasdale, ii, 705.
Louïse, E., and E. Sauvage, ii, 722.
Lucas, A. See C. Marie.
Ludlam, E. B. See G. Preuner.

M.

Macallum, A. B., ii, 708.
Maccioni, E. See E. Puxeddu.
McCrea, R. H., and A. Wilson, ii, 679.

Mailhe, A. See P. Sabatier.
Maire, M. See E. E. Blaise.
Malfitano, G., and L. Michel, ii, 692.
Malherbe, P., ii, 719.
Manasse, W. See H. Leuchs.
Mandel, J. A., and P. A. Levene, i, 807.
Marie, C., ii, 698.
Marie, C., and A. Lucas, ii, 717.
Marino, L., ii, 690, 720.
Marino, L., and G. Sericano, i, 810.
Marsden, E. G. See E. C. C. Baly.
Marshall, H., and A. T. Cameron, TRANS., 1519.
Marshall, J., ii, 722.
Marshall, J. See also L. A. Ryan.
Mascarelli, L., and A. Blasi, ii, 722.
Masson, O., TRANS., 1449.
Mathewson, C. H., ii, 682.
Mayerhofer, E., i, 780.
Mazzucchelli, A., i, 748.
Meldola, R., and J. G. Hay, TRANS., 1474.
Meyer, A. See A. Wahl.
Meyer, G. M., ii, 712.
Meyer, S., and E. von Schweidler, ii, 664.
Michaelis, L. See E. Abderhalden.
Michel, L. See G. Malfitano.
Micklethwait, F. M. G. See G. T. Morgan.
Miers, H. A., and Miss F. Isaac, ii, 670.
Mohs, K. See C. Tubandt.
Moor, W. O., ii, 709.
Morgan, G. T., and J. M. Hird, TRANS., 1505.
Morgan, G. T., and F. M. G. Micklethwait, TRANS., 1512.
Muir, M. M. P., TRANS., 1485.
Mutermilch, W. See G. Bertrand.

N.

Naoúm, P. See H. Stobbe.
Neubauer, O., and L. Flatow, i, 771.
Nicolle, M., and A. Frouin, ii, 713.
Nötzel, O. See G. Heller.
Nover, W., i, 787.
Nürnberg, A., i, 805.

O.

Orndorff, W. R., and B. J. Ray, i 800.
Orton, K. J. P., and W. W. Reed, TRANS., 1554.
Orton, K. J. P. See W. W. Reed.
Osborne, T. B., and S. H. Clapp, i, 806.
Osborne, T. B., and I. F. Harris ii, 715.

P.

Palmer, H. E. See P. E. Browning.
Paolini, V., i, 788.
Passerini, N., i, 750.
Paterno, E., and M. Cingolani, ii, 713.
Pauli, W., i, 802.
Pélabon, H., ii, 688.
Pelet, L., and E. Gillièron, i, 787.
Pfeiffer, P., ii, 694.
Ponzio, G., i, 744.
Portevin, A., ii, 694.
Pozzi-Escot, M. E., ii, 724.
Preuner, G., ii, 665.
Preuner, G., and E. B. Ludlam, ii, 665.
Prior, G. T. See G. F. H. Smith, and L. J. Spencer.
Puxeddu, E., and E. Maccioni, i, 798.

Q.

Quartaroli, A., ii, 673.

R.

Rabe, P., i, 790.
Ramsay, Sir W. See A. T. Cameron.
Ray, B. J. See W. R. Orndorff.
Recoura, A., ii, 693.
Redwood, Sir B., ii, 698.
Reed, H. S. See O. Schreiner.
Reed, W. W., and K. J. P. Orton, TRANS., 1543
Reed, W. W. See K. J. P. Orton.
Reichard, C., ii, 691.
Reitter, H., and A. Weindel, i, 748.
Richard, A., i, 755.
Richards, T. W., and G. S. Forbes, ii, 685.
Richards, T. W., and G. Jones, ii, 685.
Roehl, W., ii, 707.
Rosemann, R., ii, 706.
Rosenbloom, J., and W. J. Gies, i, 806.
Roth, P. See L. Knorr.
Rupp, E., ii, 720.
Ryan, L. A., and J. Marshall, ii, 722.
Ryder, C. T. See L. J. Henderson.

S.

Sabatier, P., and A. Mailhe, i, 747.
Sachs, F., and W. Brunetti, i, 756.
Sageman, P. J. See J. Holmes.
Salvadori, R., and C. Speroni, ii, 686.
Samec, M., i, 746.
Sasaki, T., i, 776.
Sauvage, E. See E. Louïse.
Scaffidi, V., i, 804.
Schall, R. See J. Schmidt.
Scheunert, A., and R. Bergholtz, ii, 711.
Schimmel and Co., i, 782.
Schmidt, J., and R. Schall, i, 792.
Schorigin, P., i, 753.
Schreiner, O., and H. S. Reed, ii, 715.
Schreiner, O., and E. C. Shorey, ii, 716.
Schreiner, O., and M. X. Sullivan, ii, 715.
Schweidler, E. von. See S. Meyer.
Scordo, F., ii, 713.
Semmler, F. W., i, 781.
Sericano, G. See L. Marino.
Shaffer, P., ii, 707.
Shorey, E. C. See O. Schreiner.
Sigmond, A. de, ii, 717.
Sirkar, A. P. See E. G. Hill.
Skraup, Z. H., and R. Witt, i, 806.
Smith, E. F. See L. G. Kollock, and E. T. Wherry.
Smith, G. F. H. See G. S. Blake.
Smith, G. F. H., and G. T. Prior, ii, 699.
Sokownin, N. See A. Faworsky.
Sommerfeldt, E., ii, 703.
Spencer, L. J., and G. T. Prior, ii, 700.
Speroni, C. See R. Salvadori.
Spitalsky, E., ii, 695.
Stewart, A. W., TRANS., 1537.
Stobbe, H., F. Gollücke, and W. Keding, i, 765.
Stobbe, H., W. Keding, P. Naoúm, and V. von Vigier, i, 769.
Sullivan, M. X. See O. Schreiner.
Sury, J. von, ii, 662.
Szreter, I., i, 807.

T.

Taboury, F. See F. Bodroux.
Tafel, J., i, 748.
Tafel, J., and H. Hahl, i, 765.
Tagliavini, A., ii, 721.
Tarugi, N., ii, 719.
Thien, O. See F. Kaufler.
Thiéry, ii, 723.
Tolstopjatoff, W. See A. Faworsky.
Trillat, A., ii, 716.
Truchot, P., ii, 719.
Tschirwinsky, P., ii, 705.
Tsvett, M., i, 787.
Tubandt, C., and K. Mohs, ii, 670.
Tuck, W. B. See E. C. C. Baly.
Tutton, A. E. H., ii, 688.

V.

Vaughan, V. C., ii, 712.
Verda, A., ii, 690.
Vernon, H. M., ii, 711.
Vigier, V. von. See H. Stobbe.
Voegtlin, C., ii, 710.
Voitinovici, A. See E. Abderhalden.
Vries, H. J. F. de, ii, 719.

W.

Wahl, A., and A. Meyer, i, 765.
Walden, P., i, 752.
Walter, H., ii, 681.
Walter, H. See also R. Wegscheider.
Walter, P. See R. Anschütz.
Wartenberg, H. von, ii, 697.
Webster, M. H., ii, 724.
Wegscheider, R., ii, 682.
Wegscheider, R., and H. Walter, ii, 686.
Weindel, A. See H. Reitter.
Weizmann, C. See W. H. Bentley, and A. Friedl.
Welker, W. H., ii, 721.
Wells, H. G., ii, 710.
Wherry, E. T., and E. F. Smith, ii, 721.
Whitehouse, N., ii, 680.
Willstätter, R., and F. Hocheder, i, 784.
Wilson, A. See R. H. McCrea.
Winternitz, H. See W. Caspari.
Witt, R. See Z. H. Skraup.
Wolf, C. G. L. See A. Lambert.
Wolff, J. See A. Fernbach.
Woog, P., i, 753.
Wyler, M. See A. Friedl.

Z.

Zambonini, F., ii, 663.
Zecchini, F., ii, 681.
Zelinsky, N. D., i, 780.
Žinewsky, N. See A. Faworsky.
Zöller, H. See K. Brand.

ERRATA.

VOL. XCI (TRANS., 1907).

Page	Line	
1375	2*	*for* "t" *read* "t_2."
1376	2* and 11*	in equation, *for* "t_1, t_2, and t_3" *read* "z_1, z_2, and z_3" respectively.
1377		in equation (19), in right hand expression, *for* "$=$" *read* "$-$," and in equation (21*a*), in left hand expression, *for* "k''" *read* "k_2''."

VOL. XCII (ABSTR., 1907).

PART I.

Page	Line	
509	5	*after* "forms" *insert* "the corresponding amide. The urethane prepared from this has b. p. 123°/12 mm., m. p. 60—61°, and on distillation with lime furnishes."
509	6 and 7	*delete* "the urethane has b. p. 123°/12 mm., m. p. 60—61°."

---

* From bottom.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

CLIV.—Benzoflavol (2 : 8-Dihydroxy-5-phenyl-3 : 7-dimethylacridine). By ALBERT ERNEST DUNSTAN and LOUISA CLEAVERLEY 1619

CLV.—Researches on Anthraquinones and Phthaleins. By WILLIAM HENRY BENTLEY, HENRY DENT GARDNER, jun., and CHARLES WEIZMANN 1626

CLVI.—The Velocity and Mechanism of the Reaction between Iodine and Hypophosphorous Acid. By BERTRAM DILLON STEELE 1641

CLVII.—The Action of Bromine on 5-Phenylacridine and its Halogen Derivatives. By ALBERT ERNEST DUNSTAN and THOMAS PERCY HILDITCH 1659

CLVIII.—The Adsorption of Iodine by Carbon. By OLIVER CHARLES MINTY DAVIS 1666

CLIX.—Adsorption Formulæ. By JAMES W. MCBAIN . . . 1683

CLX.—The Formation and Reactions of Imino-compounds. Part V. The Formation of Methyl Derivatives of 1 : 3-Naphthylenediamine from the Three Tolylacetonitriles. By ERNEST FRANCIS JOSEPH ATKINSON and JOCELYN FIELD THORPE 1687

CLXI.—The Atomic Volumes of Phosphorus. By EDMUND BRYDGES RUDHALL PRIDEAUX, M.A., D.Sc. 1711

CLXII.—Indican. Part I. By ARTHUR GEORGE PERKIN and WILLIAM POPPLEWELL BLOXAM 1715

CLXIII.—The Relation between Viscosity and Chemical Constitution. Part I. The Viscosity of Pyridine Solutions. By ALBERT ERNEST DUNSTAN, FERDINAND BERNARD THEODORE THOLE, and JOHN SAMUEL HUNT 1728

CLXIV.—Experiments on the Synthesis of the Terpenes. Part XI. Synthesis of 4-*iso*Propylidene*cyclo*hexanone and its Derivatives. By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN 1736

THE FARADAY LECTURE.—Synthetical Chemistry in its Relation to Biology. By EMIL FISCHER, F.R.S. 1749

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E., B. Bloch, and P. Rona, ii, 800.
Abderhalden, E., and Y. Hämäläinen, i, 831.
Abensour, J., ii, 826.
Ahrens, F. B., and J. Riemer, i, 813.
Alberda van Ekenstein, W., and J. J. Blanksma, i, 829.
Alleman, G. See L. T. Sherwood.
Amberg, S., and W. P. Morrill, ii, 799.
Andréeff, G. See A. Saytzeff.
Angelico, F., and A. Pitini, ii, 801.
Angelucci, O., ii, 773.
Arcangeli, A., ii, 813.
Arndt, K., ii, 745.
Atkinson, E. F. J., and J. F. Thorpe, TRANS., 1687.

B.

Bader, W. See F. Ullmann,
Bässler, P. See F. Kretschmer.
Banzhaf, E. J., and R. B. Gibson, i, 884.
Barbier, P., and V. Grignard, i, 852.
Barbieri, G. A., ii, 767.
Bargellini, G., i, 862.
Barker, H. C., ii, 739.
Barkla, C. G., and C. A. Sadler, ii, 731.
Bartal, A. von, ii, 775.
Baud, E., ii, 761.
Becht, F. C. See C. A. Carlson.
Beck, K., and P. Hase, i, 825.
Beckmann, E., ii, 739.
Beckmann, E., and J. Scheiber, i, 829.
Bellia, C., ii, 732.
Benecke, W., ii, 808.
Benedict, S. R., ii, 821.
Bennesch, E. See R. Kremann.
Benson, H. K. See J. L. R. Morgan.
Bentley, W. H., H. D. Gardner, jun., and C. Weizmann, TRANS., 1626.
Berghaus, ii, 803.
Berthelot, D., ii, 740.
Besson, A., ii, 811.
Betti, M., i, 854 ; ii, 726.
Binet du Jassonneix, A., ii, 779.
Blaise, E. E., i, 834.
Blanksma, J. J. See W. Alberda van Ekenstein.
Bloch, B. See E. Abderhalden.
Bloxam, W. P. See A. G. Perkin.
Bodenstein, M., and C. G. Fink, ii, 749, 750.
Boedtker, E., i, 857.
Bömer, A., G. Heimsoth, and A. Schemm, i, 820.
Böeseken, J., i, 855 ; ii, 760.
Bogdan, P., ii, 734.
Bogojawlenski, A., P. Bogoljuboff, and N. Winògradoff, ii, 745.
Bogojawlenski, A., and N. Sacharoff, ii, 751.
Bogojawlenski, A., and N. Winògradoff, ii, 752.
Bogoljuboff, P. See A. Bogojawlenski.
Bollenbach, H., ii, 820.
Boltwood, B. B., ii, 731.
Bonamartini, G., i, 883.
Bongiovanni, C., i, 833.
Borelli, V., ii, 816, 825.
Bose, E., ii, 735.
Bougault, J., ii, 828.
Bourdier, L., i, 864.
Bourion, F., ii, 773.
Bragg, W. H., and W. T. Cooke, ii, 733.
Briner, E., ii, 734.
Briner, E., and E. Durand, ii, 759.

Bronstein, G., i, 848.
Brownlee, R. H., ii, 757.
Brückner, C., ii, 772.
Bruno, A., ii, 756.
Burlingham, G. S., ii, 806.

C.

Cahn-Speyer, P., i, 849.
Carapelle, E., i, 884.
Carlson, A. J., F. C. Becht, and J. R. Greer, ii, 798.
Castoro, N., ii, 806.
Cathcart, E. P., and C. E. Fawsitt, ii, 794.
Cervello, V., and A. Pitini, i, 828.
Chapin, W. H., ii, 819.
Chappel, E. J. See W. A. H. Naylor.
Charabot, E., and G. Laloue, ii, 807.
Charrier, G., i, 829.
Charrier, G. See also G. Ponzio.
Chodat, R., and W. Staub, i, 882.
Chonowsky, B. See A. Saytzeff.
Chowansky, S. See A. Saytzeff.
Chwala, A., ii, 825.
Ciusa, R., i, 853, 874.
Cleaverley, Miss L. See A. E. Dunstan.
Coffetti, G., and G. Maderna, ii, 812.
Coffetti, G. See also G. Maderna.
Cohen, L. J., ii, 780.
Collins, K. R. See R. B. Gibson.
Colson, A., ii, 780.
Combes, R., i, 839.
Conti, C., ii, 822.
Cooke, W. T. See W. H. Bragg.
Cormimbœuf, H., ii, 810.
Cotton, A., and H. Mouton, ii, 727.
Crewe, P. H., ii, 817.
Curie, Mme. M., ii, 728, 729.

D.

Davis, O. C. M., Trans., 1666.
Dean, G. W., ii, 818.
Decolle, W. See R. Kremann.
Dehn, W. M., ii, 755.
Dehn, W. M., and E. O. Heuse, ii, 766.
Delage, Y., ii, 799.
Demierre, H., and M. Duboux, i, 833.
Deming, C. D. See I. K. Phelps.
Deventer, C. M. van, ii, 812.
Dhéré, C., ii, 726.
Di Donna, A., ii, 821.
Dieterle, P. See F. Ullmann.
Ditz, H., i, 829.
Doerinckel, F., ii, 785.
Donau, J. See F. Emich.
Donk, A. D., i, 819, 831.
Dons, R. K., ii, 824.
Dreyer, G., and O. Hansson, i, 883.
Drushel, W. A., ii, 816.
Duboux, M. See H. Demierre.
Ducelliez, F., ii, 779.
Dumansky, A. V., ii, 778.
Dunbar, P. B. See H. N. Morse.
Dunstan, A. E., and Miss L. Cleaverley, Trans., 1619.
Dunstan, A. E., and T. P. Hilditch, Trans., 1659.
Dunstan, A. E., F. B. T. Thole, and J. S. Hunt, Trans., 1728.
Durand, E. See E. Briner.

E.

Eck, P. N. van, ii, 728.
Efremoff, N. N. See S. F. Schemtschuschny.
Ehrlich, R. See R. Kremann.
Emich, F., and J. Donau, ii, 809.
Enoch, C., ii, 816.
Eve, A. S., ii, 733.
Eve, A. S., and D. McIntosh, ii, 729.

F.

Falta, W., F. Grote, and R. Staehelin, ii, 796.
Fawsitt, C. E. See E. P. Cathcart.
Fenyvessy, B. von, ii, 792.
Fetterolf, D. W., ii, 825.
Filippi, F. de, ii, 794.
Finger, H., i, 876.
Finger, H., L. Schupp, and W. Zeh, i, 876.
Fink, C. G. See M. Bodenstein.
Fischer, E., Trans., 1749.
Fischer, M. H., and G. Moore, ii, 798.
Flack, M. See L. E. Hill.
Flooh, A. See R. Kremann.
Florence, A., ii, 827.
Flürscheim, B., i, 834, 835.
Fokin, S., i, 819, 820.
Ford, W. W. See H. Schlesinger.
Fourneau, E., and M. Tiffeneau, i, 817.
Fowler, A., ii, 726.
Fraenckel, F., ii, 778.
Fränkel, W., ii, 746.
Franchimont, A. P. N., and H. Friedmann, i, 832, 877.
Franchimont, A. P. N., H. Friedmann, and W. van Rijn, i, 842.
Franke, A., M. Kohn, J. Kovačević, and J. Nemlich, i, 816.

Franklin, E. C., ii, 768.
Franzen, H., i, 880.
Frazer, J. C. W. See H. N. Morse.
Friedländer, P., i, 867.
Friedländer, P., and V. Laske, i, 848.
Friedmann, H. See A. P. N. Franchimont.
Fromm, E., and D. von Göncz, i, 872.
Fürth, O. von, and E. Jerusalem, ii, 797.
Fuld, E., and J. Wohlgemuth, ii, 797.

G.

Gardner, H. D., jun. See W. H. Bentley.
Gardner, J. A., and G. D. Knox, ii, 795.
Garnier, C. See J. de Kowalski.
Gaudechon, H., ii, 738.
Getman, F. H., ii, 744.
Geuter, P., ii, 725.
Gibson, R. B., and K. R. Collins, i, 884.
Gibson, R. B. See also E. J. Banzhaf.
Gies, W. J. See C. E. May.
Godchot, M., i, 836, 840, 841, 849.
Göncz, D. von. See E. Fromm.
Goldstein, E., ii, 725.
Gonnermann, M., ii, 801.
Gooch, F. A., and R. W. Osborne, ii, 776.
Grafe, E., ii, 796.
Gramont, A. de, ii, 788.
Grandmougin, E., i, 850.
Grau, A., and F. Russ, ii, 753.
Greer, J. R. See A. J. Carlson.
Grignard, V. See P. Barbier.
Groschuff, E. See F. Mylius.
Grossmann, H., and B. Schück, ii, 819.
Grote, F. See W. Falta.
Grünbaum, A. S., ii, 793.
Guillet, L., ii, 778, 784.
Guinchant, J., ii, 737.
Gulewitsch, W. von, i, 870.
Gutmann, A., ii, 812.

H.

Haehn, H. See K. Kof.
Hämäläinen, Y. See E. Abderhalden.
Hale, F. E., ii, 815, 821.
Hanssen, O. See G. Dreyer.
Hartley, P., ii, 795.
Hartwell, B. L., and J. W. Kellogg, ii, 808.
Hase, P. See K. Beck.
Haskins, H. D., ii, 793.
Hawley, L. F., ii, 770.
Heim, F. See J. Meisenheimer.
Heimsoth, G. See A. Bömer.
Hendrick, J., ii, 815.
Henry, L., i, 817.
Heramhof, H. See W. Muthmann.
Hérissey, H., i, 863.
Herzog, R. O., and F. Hörth, ii, 804.
Heuse, E. O. See W. M. Dehn.
Heyl, F. W. See T. B. Johnson.
Hildebrandt, H., i, 869.
Hilditch, T. P. See A. E. Dunstan.
Hill, L. E., and M. Flack, ii, 792.
Hillebrand, W. F., ii, 788.
Hillebrand, W. F., and W. T. Schaller, ii, 788.
Hinrichsen, F. W., ii, 820.
Hörth, F. See R. O. Herzog.
Hoffmann, M. See F. Kretschner.
Hoffmann, W. See F. Rothenbach.
Hofmann, K. B., and F. Pregl, i, 884.
Hoz, H. See F. Ullmann.
Hüttinger, K. See R. Kremann.
Hunt, J. S. See A. E. Dunstan.

I.

Iguchi, R. See T. Kikkoji.
Ince, W. H. See E. A. Mann.
Ipatieff, W. N., i, 827, 828.
Isaac, E., and G. Tammann, ii, 777, 786.

J.

Jackson, C. L., and R. D. MacLaurin, i, 856.
Jaeger, F. M., ii, 751.
Jaeggy, E., ii, 797.
Jänecke, E., ii, 766.
Jaques, A., i, 817.
Jerusalem, E. See O. von Fürth.
Jochelson, L. See J. Meisenheimer.
Johnson, C. M., ii, 819.
Johnson, T. B., i, 879.
Johnson, T. B., and F. W. Heyl, i, 877.
Johnson, T. B. See also H. L. Wheeler.
Johnson, W. A. See J. H. Long.
Jorissen, W. P., and W. E. Ringer, ii, 781.
Jüptner, H. von, ii, 736, 742.
Jungfleisch, E., ii, 761.

K.

Kailan, A., i, 814, 849.
Karasseff. See L. Tschugaeff.
Karl, G. See A. Pictet.
Kellner, O., ii, 794.
Kellogg, J. W. See B. L. Hartwell.
Kerschbaum, F. See R. Kremann.
Kikkoji, T., and R. Iguchi, ii, 799.
Kipper, H. See F. Ullmann.
Klobb, T., i, 864.
Knox, G. D. See J. A. Gardner.
Körbs, A., ii, 787.
Kof, K., and H. Haehn, ii, 732.
Kohn, M. See A. Franke.
Kohn, S., ii, 814.
Kolowrat, L., ii, 729.
Konstantinoff, N. C., ii, 779.
Korschun, S., ii, 821.
Kovačević, J. See A. Franke.
Kowalski, J. de, and C. Garnier, ii, 727.
Kozniewski, T., and L. Marchlewski, i, 866.
Kremann, R., ii, 747.
Kremann, R., E. Bennesch, A. Flooh, and F. Kerschbaum, i, 818.
Kremann, R., and W. Decolle, ii, 756.
Kremann, R., and R. Ehrlich, ii, 747.
Kremann, R., and K. Hüttinger, ii, 758.
Kremann, R., and F. Kerschbaum, ii, 737.
Krenner, J., ii, 790.
Kretschmer, F., P. Bässler, M. Hoffmann, H. C. Müller, and H. Römer, ii, 809.
Kruys, M. J. van't, ii, 814.
Kržižan, R., i, 821.
Kusnetzoff, P., ii, 809.

L.

Laloue, G. See E. Charabot.
Lang, W. R. See R. J. Manning.
Laske, V. See P. Friedländer.
Le Bas, G., ii, 754.
Lebeau, P., and A. Novitzky, ii, 784.
Lefebvre, C., i, 864.
Lemoult, P., ii, 760.
Lesser, E. J., ii, 827.
Levi, M. G., and E. Migliorini, ii, 756.
Lewis, G. N., ii, 735.
Leys, A., i, 822.
Lintner, C. J., ii, 823.
Loebe, R., ii, 735.
Loew, O., ii, 801.
Long, J. H., and W. A. Johnson, ii, 799.
Lorenz, R., ii, 735.
Lunjack, A. See A. Saytzeff.
Lusk, G., ii, 799.
Luther, R., and T. F. Rutter, ii, 810.
Lyford, C. A., i, 823.

M.

McBain, J. W., TRANS., 1683.
Macdonald, J. S., ii, 799.
McIntosh, D. See A. S. Eve.
Mackenzie, T. D. See F. Soddy.
MacLaurin, R. D. See C. L. Jackson.
Maclean, H., ii, 822.
McLennan, J. C., ii, 731.
Macleod, J. J. R., ii, 793, 800.
Maderna, G., and G. Coffetti, ii, 812.
Maderna, G. See also G. Coffetti.
Mai, A. See W. Muthmann.
Mann, E. A., and W. H. Ince, i, 871.
Manning, R. J., and W. R. Lang, ii, 813.
Marchionneschi, M., i, 824.
Marchlewski, L., i, 867.
Marchlewski, L. See also T. Kózniewski.
Martin, H. G., ii, 817.
Maselli, C., i, 832.
Mawrow, F., ii, 782.
May, C. E., and W. J. Gies, ii, 826.
Mdivani, B., ii, 782.
Meisenheimer, J., F. Heim, and L. Jochelson, i, 848.
Menschutkin, B. N., ii, 751.
Metzger, J. See W. Muthmann.
Meyer, J., i, 819; ii, 753.
Meyer, O. B., ii, 800.
Meyer, V. J., i, 821.
Mieg, W. See R. Willstätter.
Mieli, A., ii, 754.
Mieli, A. See also E. Paternò.
Migliorini, E. See M. G. Levi.
Mirande, M., i, 865.
Mixter, W. G., ii, 738.
Möller, W., ii, 813.
Montagne, P. J., i, 854, 855.
Moore, G. See M. H. Fischer.
Morgan, J. L. R., and H. K. Benson, ii, 743, 747.
Morrill, W. P. See S. Amberg.
Morse, H. N., P. B. Dunbar, and J. C. W. Frazer, ii, 744.
Mottram, V. H., ii, 795.
Mouton, H. See A. Cotton.
Müller, E., ii, 771, 794.

Müller, H. C. See F. Kretschmer.
Murlin, J. R., ii, 793.
Musuroff, N. See A. Saytzeff.
Muthmann, W., H. Heramhof, and L. Weiss, ii, 726, 774.
Muthmann, W., A. Mai, and L. Weiss, ii, 781.
Muthmann, W., J. Metzger, and L. Weiss, ii, 767.
Muthmann, W., R. Riedelbauch, and L. Weiss, ii, 781.
Muthmann, W., J. Scheidemandel, and L. Weiss, ii, 772.
Mylius, F., and E. Groschuff, ii, 764.

N.

Naylor, W. A. H., and E. J. Chappel, ii, 807.
Nemlich, J. See A. Franke.
Neogi, P., ii, 772.
Nicola, F., i, 853.
Nierenstein, M. See H. E. Roaf.
Novitzky, A. See P. Lebeau.

O.

Oberhoffer, P., ii, 736.
Osborne, R. W. See F. A. Gooch.
Osborne, W. A., ii, 793.
Osterberg, E., and C. G. L. Wolf, ii, 794.
Otto, R., ii, 809.

P.

Pajetta, R., ii, 814.
Paolini, V., i, 832.
Pappadà, N., ii, 754.
Parrozzani, A. See F. Scurti.
Parsons, C. A., ii, 762.
Pastrovich, P., ii, 806.
Paternò, E., and A. Mieli, i, 815.
Paternò, E., and R. Spallino, i, 813.
Pavesi, V., i, 870.
Payne, G. A. See C. Revis.
Pellet, H., ii, 811.
Pellizzari, G., i, 873.
Pellizzari, G., and F. Roncagliolo, i, 833.
Perciabosco, F. See F. Scurti.
Perkin, A. G., and W. P. Bloxam, TRANS., 1715.
Perkin, W. H., jun., and J. L. Simonsen, TRANS., 1736.
Petroff, F. See A. Saytzeff.
Pfeiffer, P., i, 872.
Pflüger, E., ii, 796.
Phelps, I. K., and C. D. Deming, i, 832.
Phelps, I. K., and M. A. Phelps, i, 823.
Phelps, M. A. See I. K. Phelps.
Pictet, A., and G. Karl, ii, 758.
Pitini, A. See F. Angelico and V. Cervello.
Poehl, A. de, ii, 802.
Ponzio, G., and G. Charrier, i, 814, 828.
Porter, A. W., ii, 743.
Power, F. B., and A. H. Salway, ii, 807.
Pozzi-Escot, E., i, 868; ii, 810, 818.
Praetorius, A., i, 835.
Pregl, F. See K. B. Hofmann.
Prideaux, E. B. R., TRANS., 1711.
Prilerzaeff, N. A., i, 814, 816.
Pushin, N. A., ii, 774.
Puxeddu, E., i, 882.

Q.

Quartaroli, A., ii, 765.

R.

Rabe, O, ii, 769.
Raichstein, V., i, 822.
Rasetti, G. See F. Ullmann.
Reich, A. See A. Stutzer.
Reimer, M., i, 852.
Reiter, K. See L. Weiss.
Rengade, E., ii, 787.
Revis, C., and G. A. Payne, ii, 823.
Rhodin, J. G. A., ii, 744.
Riedelbauch, R. See W. Muthmann.
Riehl, M. See E. Weinland.
Riemer, J. See F. B. Ahrens.
Rijn, W. van. See A. P. N. Franchimont.
Ringer, W. E. See W. P. Jorissen.
Ritzel, A., ii, 740.
Rivers, W. H. R., and H. N. Webber, ii, 800.
Rivier, H., i, 837.
Roaf, H. E., and M. Nierenstein, ii, 801.
Römer, H. See F. Kretschmer.
Rolla, L., i, 875.
Rona, P. See E. Abderhalden.
Roncagliolo, F. See G. Pellizzari.
Rosinger, H., i, 824.
Rothenbach, F., and W. Hoffmann, ii, 805.
Rubner, M., ii, 820.
Russ, F. See A. Grau.

Rutter, T. F. See R. Luther.
Rykovkoff, A. See F. Schemtschuschny.
Rywosch, D., and M. Rywosch, ii, 804.
Rywosch, M. See D. Rywosch.

S.

Sacharoff, N. See A. Bogojawlenski.
Sachs, A., ii, 791.
Sadler, C. A. See C. G. Barkla.
Salvadori, R., ii, 759.
Salway, A. H., and W. Thomas, ii, 807.
Salway, A. H. See also F. B. Power.
Sand, J., i, 814.
Saytzeff, A., G. Andréeff, B. Chonowsky, S. Chowansky, A. Lungjack, N. Musuroff, and F. Petroff, i, 815.
Scarpa, O., ii, 760.
Schaller, W. T., ii, 790.
Schaller, W. T. See also W. F. Hillebrand.
Scheiber, J. See E. Beckmann.
Scheidemandel, J. See W. Muthmann.
Schemm, A. See A. Bömer.
Schemtschuschny, S. F., and N. N. Efremoff, ii, 777.
Schemtschuschny, S. F., A. Rykovkoff, and G. Urazoff, ii, 777.
Scheringa, K., ii, 823.
Schindelmeiser, I., i, 863.
Schlesinger, H., and W. W. Ford, i, 870.
Schück, B. See H. Grossmann.
Schultze, F. See P. Wagner.
Schulz, I. A. B., ii, 798.
Schulze, E., ii, 806, 822.
Schumm, O., ii, 827.
Schupbach, A., ii, 796.
Schupp, L. See H. Finger.
Scurti, F., and A. Parrozzani, ii, 802, 803.
Scurti, F., and F. Perciabosco, i, 821.
Seidell, A., ii, 745.
Sherman, H. C., and J. E. Sinclair, ii, 793.
Sherwood, L. T., and G. Alleman, ii, 816.
Siegfried, M., ii, 825.
Sieverts, A., ii, 741.
Simonsen, J. L. See W. H. Perkin, jun.
Sinclair, J. E. See H. C. Sherman.
Smith, B. H., ii, 805.
Soddy, F., and T. D. Mackenzie, ii, 730.
Solonina, B., i, 838.
Spallino, R., i, 872.
Spallino, R. See also E. Paternò.
Spica, M., ii, 803.
Stachelin, R. See W. Falta.
Staub, W. See R. Chodat.
Steele, B. D., TRANS., 1641.
Stein, G., ii, 763.
Stortenbeker, W., ii, 764, 770.
Storz, L. See R. F. Weinland.
Straub, W., ii, 801.
Strutt, R. J., ii, 791.
Stutzer, A., and A. Reich, ii, 791.
Suzuki, S., ii, 805.
Szilárd, B., ii, 731, 757.

T.

Taboury, F., i, 837.
Tambon, J., ii, 815.
Tammann, G. See E. Isaac.
Tedesco, E. See F. Ullmann.
Thiele, F. H., ii, 798.
Thole, F. B. T. See A. E. Dunstan.
Thomas, W. See A. H. Salway.
Thorpe, J. F. See E. F. J. Atkinson.
Tichomiroff, V., ii, 752.
Tiffeneau, M. See E. Fourneau.
Tingle, J. B., i, 882.
Tschugaeff, L., and Karassoff, i, 830.

U.

Ulffers, F., ii, 776.
Ullmann, F., W. Bader, P. Dieterle, H. Hoz, H. Kipper, G. Rasetti, and E. Tedesco, i, 842.
Ullmann, F., and C. Wagner, i, 846.
Urazoff, G. See S. F. Schemtschuschny.

V.

Valeton, J. J. P., ii, 811.
Vandevelde, A. J. J., ii, 792.
Vanzetti, B. L., i, 823.
Vegesack, A. von, ii, 769.
Vetere, V., ii, 811.
Vicario, A., ii, 772.
Victoroff, C., ii, 822.
Vigouroux, E., ii, 767, 780, 785.
Voerman, G. L., i, 868.

W.

Wagner, B., and F. Schultze, ii, 814, 821.
Wagner, C. See F. Ullmann.

Wald, F., ii, 755.
Walden, P., ii, 784.
Wallis, T. E., ii, 820.
Warren, W. H., and R. S. Weiss, i, 869.
Webber, H. N. See W. H. R. Rivers.
Wegscheider, R., i, 850.
Weinland, E., and M. Riehl, ii, 796.
Weinland, R. F., and L. Storz, ii, 771.
Weiss, L., and K. Reiter, i, 841.
Weiss, L. See W. Muthmann.
Weiss, R. S. See W. H. Warren.
Weizmann, C. See W. H. Bentley.
Weston, R. S., ii, 817.
Wheeler, H. L., i, 879.
Wheeler, H. L., and T. B. Johnson, ii, 826.
Wilfarth, H., and G. Wimmer, ii, 809.
Williams, R. S., ii, 783.
Willstätter, R., and W. Mieg, i, 865.
Wilson, T. M., ii, 792.
Wimmer, G. See H. Wilfarth.
Winogradoff, N. See A. Bogojawlenski.
Wohlgemuth, J. See E. Fuld.
Wolf, C. G. L. See E. Osterberg.

Z.

Zavrieff, D., ii, 768.
Zeh, W. See H. Finger.

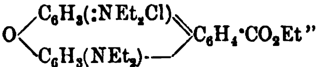
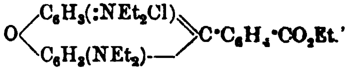
ERRATA.

VOL. XCI (TRANS., 1907).

Page	Line	
1531	18	*for* "B" *read* "β".

VOL. XCII (ABSTR., 1907).

PART I.

232	21	,, "MEEGEN" *read* "MEIGEN."
606	15*	,, "2 : 2′ : 5 : 5′-*Tetramethoxybenzylideneazine*" *read* "2 : 2′ : 5 : 5′-*Tetramethoxydibenzylideneazine*."
619	13	,, "1-*Methyl*cyclo*hexyl*-4-*acetamide*" *read* "1-*Methyl*cyclo*hexene*-4-*acetamide*."
726	17*	,, "  " *read* "  '

PART II.

946 col. i l. 26 *for* "A. ii, 974" *read* "A, i, 974."

---

* From bottom.

In Column II, x represents the expansion by volume appertaining to the molecular mixture K_2SO_4,H_2SO_4, and by substituting for x the value determined for it above, namely, $2 \times 3{\cdot}94$, we are enabled to calculate the expansions yielded at the different concentrations in mixtures of 100 gram-molecules (Column III). These are identical with the values obtained for aqueous potassium sulphate and sulphuric acid mixtures (p. 1614).

Further evidence in support of this theory is afforded when we consider the nature of the volumetric changes in aqueous mixtures, in which these changes can be referred almost exclusively to chemical forces.

The change in volume, being in these circumstances a rectilinear function of the intensity of chemical affinity, should accord with the expression:

$$\xi = \beta . K,$$

where ξ is the change in volume and β the number of molecules which have combined chemically.

The following results were obtained by mixing normal solutions of hydrochloric acid and sodium hydroxide:

Volume of *N*-sodium hydroxide mixed with 100 volumes of *N*-hydrochloric acid.	Expansion in volume.
12·59	0·251
25·17	0·495
33·51	0·657
49·68	0·976
100·57	1·978
202·10	1·934
299·74	1·916
402·66	1·887
803·50	1·862

Calculating as before from the expansion curves, the following figures are obtained for mixtures of 100 gram-molecules of alkali and acid:

I. Number of gram-molecules of hydrochloric acid in the initial volumes.	II. Number of molecules which have combined chemically.	III. Expansion. (*a*.) Observed.	(*b*.) Calculated from the expression: $\xi = \beta . K$.
88·9	22·2	223	218
80·0	40·0	395	394
75·0	50·0	490	492
66·7	66·7	653	656
50·0	100·0	984	—
33·3	66·7	644	656
25·0	50·0	479	492
20·0	40·0	377	394
11·1	22·2	207	218

When these expansions are plotted similarly to those obtained in the case of aqueous mixtures of sulphuric acid with its neutral salts (Fig. 2), the difference between chemical and physical forces in solution are more clearly seen.

It would appear from these considerations that the volumetric changes obtained when sulphuric acid and its neutral salts are mixed together in aqueous solution result from the action of physical forces inherent to the molecules, and are independent of chemical affinity (so-called) and the formation of acid sulphates. It follows therefore that in such mixtures the relative complexities of the interacting molecules can be deduced from a comparison of the volumetric changes at corresponding molecular mixtures and the weights of the bodies which yield a maximum deviation from the theoretical.

It is apparent from a consideration of the molecular expansion curves in the case of mixtures of sulphuric acid with the sulphates of potassium, sodium, ammonium, magnesium, zinc, and copper, that these substances are similarly aggregated in solution. In the case of aluminium sulphate, however, on the assumption that its molecule can be represented by $Al_2(SO_4)_3$, as compared with H_2SO_4 for the molecule of sulphuric acid, the expansions at corresponding concentrations are not comparable, and the maximum occurs at the molecular mixture $Al_2(SO_4)_3,2H_2SO_4$. The molecule of sulphuric acid must therefore be represented by $(H_2SO_4)_2$ if that of aluminium sulphate is $Al_2(SO_4)_3$, and confirmation of this is afforded when the changes in volume are calculated according to this view (Column VII*b*).

Many additional mixtures were made with a view to eliminating the slight differences between the observed and calculated expansion curves. From the fact, however, that the contraction curves of water with the several constituents of the mixtures were not quite of the same order, this could not be done. For, although these curves could be superimposed through a considerable range without fear of the slight differences leading to discrepancies in the determination of the relative aggregations of the interacting substances, the differences between the curves increased with the distance from the point of coincidence. When attempts were made to obviate this by mixing together, at these extreme concentrations, solutions which yielded exactly the same contraction, it was found that the increased differences in the densities of the two solutions caused a still greater deviation from the theoretical, probably due to the gravitating effect of differences in mass already advanced in the case of mixtures of pure liquids. Conversely by mixing solutions containing equal proportions by weight of the interacting substances, the divergence of the two curves became more accentuated, proving that in these mixtures complete elimination of extraneous influences could not be effected.

So long, however, as the mixtures with water gave contraction curves of approximately equal slope, according to the method given above for the elimination of disturbing influences around the point of equimolecular mixtures, the molecular expansion curves obtained were practically identical at varying dilutions, proving that no breaking down of molecular complexes occurs on dilution, but that within a very considerable range each molecule retains its individuality.

It will be noticed that the method of interpreting volumetric changes here employed in cases of substances which mix together without apparent molecular change is antagonistic to the existence of hydrates in solutions of inorganic salts, just as has been already demonstrated in the case of organic solutions (*loc. cit.*). The neutral anhydrous sulphates of potassium and ammonium, for instance, give with sulphuric acid a maximum expansion at the same molecular mixtures as the variably hydrated sulphates of copper, sodium, &c., whereas if the latter consisted of molecular complexes containing water chemically combined, these results would not be expected. On similar grounds, it is probable that the molecules of acid sulphates have no individual existence in aqueous solutions, but appear as mixtures of the neutral salt and sulphuric acid in molecular proportions, and this applies also to crystalline hydrated and double salts which are dependent on temperature and concentration for their composition and crystalline form.

In conclusion, we wish to express our indebtedness to Dr. Thorpe, C.B., F.R.S., for facilities afforded us in carrying on this investigation.

GOVERNMENT LABORATORY.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

CLXV.—The Occurrence of Quercitol (Quercite) in the Leaves of *Chamaerops humilis*. By **Hugo Müller** 1766

CLXVI.—Cocositol (Cocosite), a Constituent of the Leaves of *Cocos nucifera* and *Cocos plumosa*. By **Hugo Müller** . 1767

CLXVII.—Inositol (Inosite). By **Hugo Müller** . . . 1780

CLXVIII.—Hydrates of Some Quaternary Bases. By **David Cowan Crichton** (Carnegie Research Scholar) . . . 1793

CLXIX.—*para*-Toluidine Monohydrate. By **James Walker** and **Heather Henderson Beveridge** (Carnegie Research Scholar) 1797

CLXX.—The Production of Orcinol Derivatives from the Sodium Salt of Ethyl Acetoacetate by the Action of Heat. By **John Norman Collie** and **Edwin Rodney Chrystall** . 1802

CLXXI.—Derivatives of the Multiple Keten Group. By **John Norman Collie** 1806

CLXXII.—Racemisation by Alkali as Applied to the Resolution of *r*-Mandelic Acid into its Optically Active Isomerides. By **Alex. McKenzie** and **Hermann August Müller** . . 1814

CLXXIII.—The Optical Activity of Cyclic Ammonium Compounds. By **Frank Buckney**, B.A., and **Humphrey Owen Jones** 1821

CLXXIV.—Some Double Ferrocyanides of Calcium, Potassium, and Ammonium. By **James Campbell Brown**, D.Sc. . . 1826

CLXXV.—The Condensation of Acetaldehyde and its Relation to the Biochemical Synthesis of Fatty Acids. By **Henry Stanley Raper** 1831

PAGE

CLXXVI.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part X. Effect of the Configuration and Degree of Saturation of the Solvent. By **Thomas Stewart Patterson**, **Andrew Henderson**, M.A., B.Sc., and **Frank Walter Fairlie**, B.Sc. . . . 1838

CLXXVII.—Two Volumetric Methods for the Determination of Chromium. By **Arnold William Gregory**, B.Sc. (Lond.), and **James McCallum** 1846

CLXXVIII.—The Atomic Weight of Tellurium. By **Herbert Brereton Baker** and **Alexander Hutcheon Bennett** . 1849

CLXXIX.—Gaseous Nitrogen Trioxide. By **Herbert Brereton Baker**, M.A., D.Sc., F.R.S., and **Muriel Baker** . . . 1862

CLXXX.—The Decomposition of Hyponitrous Acid in Presence of Mineral Acids. By **Prafulla Chandra Rây** and **Atul Chandra Gañguli** 1866

CLXXXI.—Contributions to the Chemistry of the Terpenes. Part II. The Oxidation of Limonene with Chromyl Chloride. By **George Gerald Henderson** 1871

CLXXXII.—Studies in the Camphane Series. Part XXIV. Camphoryldithiocarbamic Acid and Camphorylthiocarbimide. By **Martin Onslow Forster** and **Thomas Jackson** . 1877

CLXXXIII.—Aromatic Amides and Imides of Camphoric Acid. By **William Ord Wootton** 1890

CLXXXIV.—Ethyl α-Cyano-γ-phenylacetoacetate. By **Arthur Richard Smith** and **Jocelyn Field Thorpe** 1899

CLXXXV.—Chemical Examination of the Root and Leaves of *Morinda longiflora*. By **Marmaduke Barrowcliff** and **Frank Tutin** 1907

CLXXXVI.—The Interaction of Cyanodihydrocarvone, Amyl Nitrite, and Sodium Ethoxide. Part II. The Constitution of the Products. By **Arthur Lapworth** and **Elkan Wechsler** 1919

CLXXXVII.—The Synthesis of Acridines and Phenonaphthacridines: Tetra- and Hexa-methylacridines: Dimethylphenonaphthacridines: Dixylylmethylenediamines. By **Alfred Senier** and **Arthur Compton** 1927

CLXXXVIII.—Keten. By **Norman Thomas Mortimer Wilsmore** 1938

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E., and H. Deetjen, ii, 889.
Abderhalden, E., and A. Gigon, ii, 892, 893.
Abderhalden, E., A. Gigon, and E. S. London, ii, 891.
Abderhalden, E., and M. Kempe, ii, 896.
Abderhalden, E., K. von Körösy, and E. S. London, ii, 893.
Abderhalden, E., E. S. London, and O. Prym, ii, 892.
Abderhalden, E., E. S. London, and C. Voegtlin, ii, 892.
Abderhalden, E., and B. Oppler, ii, 889.
Abderhalden, E., and O. Prym, ii, 897.
Abderhalden, E., and P. Rona, ii, 890, 892.
Abderhalden, E., and C. Voegtlin, ii, 893.
Abderhalden, E. See also E. Fischer.
Abegg, R., ii, 853.
Ackermann, E. See P. Rabe.
Acqua, C., ii, 904.
Acree, S. F., and J. M. Johnson, ii, 855.
Acree, S. F., and S. Nirdlinger, ii, 857.
Ahrens, F. B., and A. Luther, i, 965.
Aktien-Gesellschaft für Anilin-Fabrikation, i, 907, 925, 969, 975, 980.
Alderson, E. See H. E. Roaf.
Alfano, P. See M. Bakunin.
Allers, R. A., i, 995.
Anders, G. See W. Herz.
Anderson, C., ii, 887.
Anselmino, O., i, 913.
Archibald, E. H., ii, 840.
Arinkin, M., ii, 897, 903.
Armstrong, H. E., and R. J. Caldwell, ii, 850.
Armstrong, H. E., J. V. Eyre, A. V. Hussey, and W. P. Paddison, ii, 848.
Armstrong, H. E., and J. A. Watson, ii, 849.
Arndt, K., ii, 842.
Aron, H., i, 989.
Aschan, O., i, 947.
Ascoli, M., and G. Izar, ii, 897.
Auwers, K., i, 928.
Auwers, K., F. Jescheck, and C. Kipke, i, 917.
Auwers, K., and E. Rietz, i, 919, 938.
Azzarello, E. See A. Peratoner.

B.

Bacon, R. F., ii, 854.
Badische Anilin- & Soda-Fabrik, i, 942, 943, 973.
Baikoff, A. A., ii, 874.
Baker, H. B., and Mrs. M. Baker, Trans., 1862.
Baker, H. B., and A. H. Bennett, Trans., 1849.
Baker, Mrs. M. See H. B. Baker.
Bakunin, M., and P. Alfano, i, 915.
Bakunin, M., and C. Profilo, i, 911.
Bang, I, ii, 900.
Bang, I., V. Bohm, and M. Ljungdahl, ii, 898.
Bargellini, G., i, 931, 962.
Bargellini, G., and S. Silvestri, i, 914.
Barratt, J. O. W., and E. S. Edie, ii, 847.
Barrowcliff, M., and F. Tutin, Trans., 1907.

Bartow, E., and J. M. Lindgren, ii, 866.
Basler Chemische Fabrik, i, 920.
Baumert, R., ii, 909.
Becht, F. C. See A. J. Carlson.
Becker, C. T., and E. O. Herzog, ii, 896.
Becker, V. See R. Nietzki.
Beckmann, E., and G. Lockemann, ii, 845.
Bell, J. M., and W. C. Taber, ii, 867.
Belonowski, G., ii, 903.
Bennett, A. H. See H. B. Baker.
Bent, L. N. See W. H. Walker.
Berg, A., ii, 881.
Berl, E., and A. Rittener, ii, 864.
Berl, E. See also G. Lunge.
Beveridge, H. H. See J. Walker.
Bewad, I. J., i, 906.
Biginelli, P., i, 955.
Binz, A., and T. Marx, i, 923.
Blumann, A. See O. Wallach.
Boedecker, F. See O. Wallach.
Bogojawlensky, A. D., and N. Winogradoff, ii, 844.
Bohm, V. See I. Bang.
Bolognesi, G., ii, 901.
Boltwood, B. B., ii, 836.
Bonnet, F. See T. W. Richards.
Borsche, W., and A. Reclaire, i, 987.
Bougault, J., ii, 916.
Braun, J. von, i, 893, 899, 960.
Bredig, G., W. Fraenkel, and E. Wilke, i, 903.
Breit, E. See W. Wislicenus.
Breslauer, J., and A. Pictet, i, 915.
Breteau, P., and H. Leroux, ii, 908.
Bretin. See Evesque.
Brink, F. N. See T. W. Richards.
Brögger, W. C., ii, 884.
Brown, J. C., TRANS., 1826.
Browne, A. W., and F. F. Shetterly, ii, 863.
Bucherer, H. T., i, 981.
Buchtala, H., i, 993.
Buckney, F., and H. O. Jones, TRANS., 1821.
Bülow, C., and M. Lobeck, i, 986.
Bugge, G. See K. A. Hofmann.
Buglia, G., ii, 898.
Burgess, G. K. See C. W. Waidner.
Bywaters, H. W. See W. Wislicenus.

C.

Calcagni, G. See N. Parravano.
Caldwell, R. J. See H. E. Armstrong.
Cameron, F. K., ii, 867.
Cantone, M., ii, 829.
Carlson, A. J., F. C. Becht, and J. R. Greer, ii, 891.
Carobbio, A., ii, 916.
Cederholm, A. M. See W. H. Walker.
Centnerszwer, M., and A. Kalnin, ii, 847.
Chardin, D., and S. Sikorski, ii, 830.
Chassagne, J., i, 892.
Chattaway, F. D. See E. Cohen.
Chemische Fabrik auf Aktien (vorm. E. Schering), i, 902, 921.
Chemische Fabrik von Heyden (Aktien-Gesellschaft), i, 888, 953.
Chéneveau, C., ii, 829.
Chrystall, E. R. See J. N. Collie.
Claessen, C., i, 885.
Claisen, L., i, 940.
Clapp, S. H. See T. B. Osborne.
Clarke, T. W., and W. H. Hartley, i, 992.
Cohen, E., F. D. Chattaway, and W. Tombrock, ii, 838.
Cohnheim, O., i, 996.
Colani, A., ii, 878.
Collie, J. N., TRANS., 1806.
Collie, J. N., and E. R. Chrystall, TRANS., 1802.
Collins, S. W., ii, 907.
Colson, A., ii, 877.
Compton, A. See A. Senier.
Conduché, A. See L. J. Simon.
Conrad, M., i, 985.
Consortium für Elektrochemische Industrie. See G. Imbert.
Cooksey, C. D., ii, 837.
Cornu, F., and C. Schuster, ii, 887.
Court, G. See A. Pictet.
Crafts, J. M., ii, 855.
Crichton, D. C., TRANS., 1793.
Croner, F., i, 948.
Curry, B. E., ii, 872.
Curry, B. E., and S. H. Woods, ii, 873.
Curtius, T., i, 969.
Curtius, T., and A. Riedel, i, 970.

D.

Danaila, N. See C. Liebermann.
Dannerth, F., i, 909.
Davis, G. T. See W. M. Dehn.
Decker, H., and T. von Fellenburg, i, 950.
Deetjen, H. See E. Abderhalden.
Dehn, W. M., ii, 906.
Dehn, W. M., and G. T. Davis, i, 885.

Dennstedt, M., ii, 909.
Deussen, E., and A. Lewinsohn, i, 945.
Dickinson, H. C., and E. F. Mueller, ii, 843.
Dieckmann, W., and H. Kammerer, i, 979.
Ditte, A., ii, 862.
Dobson, M. E. See R. A. Robertson.
Dodt, J. See J. Tafel.
Dolgolenko, V. I., ii, 846.
Dombrowski, S., i, 993.
Dorn, E., ii, 837.
Dreyer, G., and O. Hanssen, ii, 835, 890.
Ducelliez, F., ii, 880.
Dumanski, A., ii, 841.

E.

Edie, E. S. See J. O. W. Barratt.
Einbeck, H. See R. Pschorr.
Embden, G., E. Liefmann, and H. Lüthje, ii, 889.
Erdmann, E., i, 968.
Evesque, Verdier, and Bretin, ii, 912.
Eyre, J. V. See H. E. Armstrong.

F.

Fabinyi, R., and T. Széki, i, 939.
Fairlie, F. W. See T. S. Patterson.
Farbenfabriken vorm. Friedr. Bayer & Co., i, 914, 942, 972, 977.
Farbwerke vorm. Meister, Lucius, & Brüning, i, 923.
Fay, H., ii, 880.
Fecht, H., i, 906, 926.
Feigl, J., ii, 891.
Feist, F., i, 949.
Fellenburg, T. von. See H. Decker.
Fichter, F., and H. Probst, i, 977.
Fischer, E., i, 901.
Fischer, E., and E. Abderhalden, i, 990.
Fischer, E., and K. Raske, i, 900.
Fischer, O., and F. Römer, i, 981.
Flooh, J. See H. Schrötter.
Forster, M. O., and T. Jackson, Trans., 1877.
Fraenkel, W. See G. Bredig.
Franchini, G., ii, 895.
Franklin, E. C., and H. D. Gibbs, ii, 840.
Freimann, H. See E. Grandmougin.
Friedländer, K., ii, 895.
Fromholdt, G., ii, 902.
Fromm, E., and E. Vetter, i, 982.
Fühner, H., ii, 901.
Fürth, O. von, and E. Jerusalem, i, 993.
Fürth, O. von, and E. Scholl, i, 994.

G.

Gañguli, A. C. See P. C. Rây.
Gesellschaft für Chemisch Industrie in Basel, i, 987.
Gibbs, H. D. See E. C. Franklin.
Gies, W. J., i, 995.
Gigon, A. See E. Abderhalden.
Glixelli, S., ii, 869.
Godet, C. See E. Schulze.
Goldschmiedt, G., i, 894, 922.
Goldschmidt, H., and O. Udby, ii, 852.
Goldsobel, A. G., i, 888.
Gorke, H. See A. Hantzsch.
Goy, S., ii, 911.
Grandmougin, E., and H. Freimann, i, 986.
Grandmougin, E., H. Freimann, and J. R. Guisan, i, 987.
Green, A. G., and P. E. King, i, 933.
Greer, J. R. See A. J. Carlson.
Gregory, A. W., and J. McCallum Trans., 1846.
Greinacher, H., ii, 836.
Greshoff, M., ii, 914.
Grimme, C. See L. Knorr.
Gruener, H., ii, 860.
Gruner, O. C., ii, 900.
Guertler, W. E., ii, 876.
Guillet, L., ii, 874.
Guisan, J. R. See E. Grandmougin.
Gutmann, A., ii, 862.

H.

Haarmann, and Reimer, i, 937.
Hackspill, L., ii, 876.
Hanssen, O. See G. Dreyer.
Hantzsch, A., ii, 834.
Hantzsch, A., H. Gorke, and Miss E. Morgan, i, 927.
Hantzsch, A. See also K. H. Meyer.
Hartley, W. H. See T. W. Clarke.
Haselhoff, E., ii, 905.
Haslinger, C., i, 975.
Hausmann, J. See R. Zaloziecki.
Hauth, A. See A. Windaus.
Heald, W., ii, 859.
Heathcote, H. L., ii, 851.
Hébert, A., ii, 902.
Hedin, S. G., ii, 891.
Henderson, A. See T. S. Patterson.
Henderson, G. G., Trans., 1871.

Henderson, L. J., ii, 846.
Henning, F. See L. Holborn.
Henrard, J. T., i, 917.
Henry, L., i, 886, 887, 898.
Hervieux, C. See C. Porcher.
Herz, W., and G. Anders, ii, 848.
Herzog, R. O. See C. T. Becker.
Heubner, W. See R. Willstätter.
Hibbert, Miss E. See E. Knecht.
Hönigschmid, O, ii, 873, 877.
Hörlein, H. See L. Knorr.
Hofbauer, J., ii, 901.
Hoffmann, A. See F. W. Semmler.
Hofmann, K. A., and G. Bugge, i, 887, 904.
Holborn, L., and F. Henning, ii, 844.
Holmes, W. B., ii, 873.
Horn, D. W., ii, 871.
Houghton, H. W., i, 996.
Houseman, P. A. See J. Tafel.
Hughes, A. L. See G. Owen.
Hussey, A. V. See H. E. Armstrong.

I.

Imbert, G., and Consortium für Elektrochemische Industrie, i, 977.
Irvine, J. C. See R. A. Robertson.
Izar, G. See M. Ascoli.

J.

Jackson, C. L., and J. E. Zanetti, ii, 859.
Jackson, T. See M. O. Forster.
Jänecke, E., ii, 870.
Jannasch, P., and W. Jilke, ii, 864.
Jensen, C., ii, 835.
Jerusalem, E. See O. von Fürth.
Jescheck, F. See K. Auwers.
Jilke, W. See P. Jannasch.
Johannsen, D. See R. Stoermer.
Johnson, J. M. See S. F. Acree.
Johnson, T. B., and L. H. Levy, i, 910.
Jolles, A., ii, 900.
Jones, H. O. See F. Buckney.
Jones, L. W., i, 897.
Jordis, E., ii, 876.
Just, G., and Terres, ii, 852.

K.

Kablukoff, I. A., ii, 865.
Kailan, A., ii, 853.
Kaiser, K., ii, 862,
Kämmerer, H. See W. Dieckmann.
Kalle and Co., i, 935, 953, 963, 983.
Kalnin, A. See M. Centnerszwer.
Kametaka, T. See R. Willstätter.
Kanewsky, I. See A. V. Saposhnikoff.
Kanolt, C. W., ii, 839.
Kastle, J. H., and J. H. McHargue, ii, 861.
Kayser, E., and H. Marchand, ii, 903.
Keim, P. See H. von Liebig.
Kempe, M. See E. Abderhalden.
Kijner, N. M., i, 935.
Kikkōji, T., ii, 898.
King, P. E. See A. G. Green.
Kipke, C. See K. Auwers.
Kirschnick, C., ii, 910.
Knaffl-Lenz, E. von, i, 994.
Knecht, E., and Miss E. Hibbert, ii, 907.
Knoll & Co., i, 958.
Knorr, L., C. Grimme, and H. Hörlein, i, 956.
Knorr, L., and R. Waentig, i, 957.
Kochmann, M., ii, 902.
Körösy, K. von. See E. Abderhalden.
Kohlrausch, F., ii, 840.
Kohn, M., i, 899.
Kohn, M., and A. Schmidt, i, 901.
Kolker, M. See S. von Kostanecki.
Konowaloff, D. P., ii, 854.
Kostanecki, S. von, C. Marschalk, and V. Lampe, i, 950.
Kostanecki, S. von, M. Kolker, H. Rabinowitsch, G. Stenzel, and A. Tobler, i, 952.
Kremann, R., i, 912.
Krüger, P. See V. Schenke.
Kruys, M. J. van't. See B. Sjollema.
Kunckell, F., and A. Richartz, i, 937.
Kurorski, E. See S. Tanatar.

L.

Ladenburg, A., i, 956.
Lagers, G. H. G., ii, 907.
Lampe, V. See S. von Kostanecki.
Lange, M., i, 930.
Langstein, L., i, 989.
Lapworth, A., and E. Wechsler, TRANS., 1919.
Laubé, E., i, 941.
Lawroff, D., i, 995.
Leavenworth, C. S. See L. B. Mendel.
Lee, F. S., ii, 898.

Leroux, H. See P. Breteau.
Letsche, E., ii, 888.
Levin, M., ii, 836.
Levites, S., ii, 891.
Levy, L. H. See T. B. Johnson.
Levy, P., i, 947.
Lewinsohn, A. See E. Deussen.
Liebermann, C., i, 955.
Liebermann, C., and N. Danaila, i, 976.
Liebermann, C., and S. Lindenbaum, i, 889.
Liebermann, C., and H. Truchsäss, i, 890.
Liebig, H. von, i, 940.
Liebig, H. von, and P. Keim, i, 930.
Liefmann, E. See G. Embden.
Liesegang, R. E., i, 993.
Lifschütz, I., ii, 899.
Lillie, R. S., ii, 847.
Limmer, F., ii, 882.
Lindenbaum, S. See C. Liebermann.
Lindgren, J. M. See E. Bartow.
Lindner, J., i, 892.
Ljungdahl, M. See I. Bang.
Lobeck, M. See C. Bülow.
Lockemann, G. See E. Beckmann.
Loeb, J., ii, 896.
Lohnstein, R., ii, 868.
London, E. S., ii, 894.
London, E. S., and W. W. Polowzowa, ii, 894.
London, E. S., and A. Sagelmann, ii, 894.
London, E. S. See also E. Abderhalden.
Long, J. H., i, 991.
Lorenz, R., and A. Mohn, ii, 838.
Lottermoser, A., ii, 851.
Luckow, C., ii, 869.
Lüthje, H. See G. Embden.
Lumière, A., L. Lumière, and A. Seyewetz, ii, 866.
Lumière, L. See A. Lumière.
Lunge, G., and E. Berl, ii, 863.
Luther, A. See F. B. Ahrens.

M.

McCallum, J. See A. W. Gregory.
McHargue, J. S. See J. H. Kastle.
McKenzie, A., and H. A. Müller, TRANS., 1814.
Maignon, F., ii, 898.
Maltese, R., i, 912.
Mansier, ii, 906.
Marchand, H. See E. Kayser.
Marchese, C., i, 941; ii, 911.
Marschalk, C. See S. von Kostanecki.
Marek, J., ii, 909.
Martinand, V., ii, 904.
Marx, K. See R. Meyer.
Marx, T. See A. Binz.
Massol, G., ii, 911.
Mauthner, J., i, 921.
Mazzucchelli, A., i, 891.
Meigen, W., i, 949.
Meillère, G., i, 893.
Meister, F. See O. Wallach.
Meister, W., i, 885.
Mendel, L. B., C. S. Leavenworth, and P. H. Mitchell, ii, 895.
Merck, E., i, 972; ii, 859.
Mestresat, W., ii, 903.
Meyer, K. H., and A. Hantzsch, i, 932.
Meyer, R., and K. Marx, i, 932.
Michaelis, A., and K. Schenk, i, 966.
Micko, K., i, 994.
Miller, W., ii, 837.
Mitchell, P. H. See L. B. Mendel.
Möller, W. See P. Pfeiffer.
Mohn, A. See R. Lorenz.
Morgan, Miss E. See A. Hantzsch.
Morgan, J. L. R., and F. T. Owen, ii, 845.
Moscati, G., ii, 898.
Mossler, G., i, 947.
Mostowitsch, W., ii, 870.
Müller, E., ii, 829.
Mueller, E. F. See H. C. Dickinson.
Müller, H., TRANS., 1766, 1767, and 1780.
Müller, H. A. See A. McKenzie.
Müller, M., ii, 895.
Murlin J. R., ii, 895.
Murmann, E., ii, 905.
Mylius, F., ii, 910.

N.

Nemser, M. H., ii, 894.
Neuberg, C., i, 995.
Neukam, H. See H. Pauly.
Nietzki, R., and V. Becker, i, 978.
Nirdlinger, S. See S. F. Acree.
Noguchi, H., ii, 890.

O.

Obermiller, J., i, 910.
Oechsner de Coninck, W., i, 927.
Opolski, S., i, 908.
Oppenheimer, S., ii, 900.
Oppler, B. See E. Abderhalden.
Orloff, E. J., i, 892.
Osborne, T. B., and S. H. Clapp, i, 990.

Ostromysslensky, I., i, 994; ii, 847, 864.
Owen, G., and A. L. Hughes, ii, 843.
Owen, F. T. See J. L. R. Morgan.

P.

Paddison, W. P. See H. E. Armstrong.
Paladino, R., 905.
Parravano, N., and G. Calcagni, ii, 870.
Parravano, N., and A. Pasta, i, 961.
Pasta, A. See N. Parravano.
Patterson, T. S., F. W. Fairlie, and A. Henderson, Trans., 1838.
Pauly, H., and K. Neukam, i, 916.
Pawloff, W. E., and S. D. Schein, ii, 906.
Pécheux, H., ii, 842.
Pegoraro, L. See G. Pellini.
Pellet, L., ii, 912.
Pellini, G., and L. Pegoraro, ii, 860.
Peratoner, A., and E. Azzarello, i, 979.
Pfeiffer, P., and W. Möller, i, 931.
Pfeiffer, P., Prade, Stern, and A. Trieschmann, i, 895.
Pfeiffer, W., ii, 899.
Philips, M., ii, 870.
Philosophoff, P., ii, 908.
Pictet, A. See J. Breslauer.
Pictet, A., and G. Court, i, 954.
Plimmer, H. G., and J. D. Thomson, ii, 903.
Pollak, L., i, 991.
Polowzowa, W. W. See E. S. London.
Polzeniusz, F. E., ii, 867.
Poni, P., ii, 883.
Popovici, J., i, 935.
Porai-Koschitz, A., P. Solodowinkoff, and M. Troitzki, i, 974.
Porcher, C., and C. Hervieux, ii, 900.
Prade. See P. Pfeiffer.
Preti, L., ii, 897, 899.
Preuner, G., ii, 861.
Probst, H. See F. Fichter.
Profilo, C. See M. Bakunin.
Prym, O. See E. Abderhalden.
Pschorr, R., and H. Einbeck, i, 958.
Pushin, N. A., ii, 837.

R.

Rabe, P., E. Ackermann, and W. Schneider, i, 954.
Rabinowitsch, H. See S. von Kostanecki.
Rakusin, M. A., ii, 882, 883.
Randall, D. L., ii, 912.
Raper, H. S., Trans., 1831.
Raschig, F., ii, 863.
Rasko, K. See E. Fischer.
Rây, P. C., and A. C. Gañguli, Trans., 1866.
Reclaire, A. See W. Borsche,
Reichard, C., ii, 914, 915.
Reimer. See Haarmann.
Reissert, A., i, 908.
Reverdin, F., i, 925.
Richards, T. W., F. N. Brink, F. Bonnet, and W. N. Stull, ii, 858.
Richardson, W. D., ii, 907.
Richartz, A. See F. Kunckell.
Riedel, A. See T. Curtius.
Riedel, J. D., i, 897, 920.
Rietz, E. See K. Auwers.
Rittener, A. See E. Berl.
Roaf, E., and E. Alderson, ii, 896.
Robertson, R. A., M. E. Dobson, and J. C. Irvine, i, 894.
Robertson, T. B., i, 990.
Römer, F. See O. Fischer.
Rona, P. See E. Abderhalden.
Rosenheim, O., and M. C. *Tebb*, i, 995.
Roure-Bertrand, jun., i, 943; ii, 905.
Rümelin, G., ii, 836.
Rusting, N., ii, 912.

S.

Sachs, F., i, 914.
Sacharoff, M. See A. V. Saposhnikoff.
Sagelmann, A. See E. S. London.
Sahmen, R., and A. von Vegesack, ii, 847.
Salomone, G., ii, 903.
Saposhnikoff, A. V., and I. Kanewsky, ii, 869.
Saposhnikoff, A. V., and M. Sacharoff, ii, 869.
Schade, H., ii, 857.
Schaposchnikoff, W., i, 948.
Schein, S. D. See W. E. Pawloff.
Schenk, K. See A. Michaelis.
Schenke, V., and P. Krüger, ii, 910.
Schmidt, A. See M. Kohn.
Schmidt, O., i, 903.
Schneider, W. See P. Rabe.
Scholl, E. See O. von Fürth.
Schrötter, H., and J. Flooh, i, 929.
Schulze, E., and C. Godet, i, 903.
Schulze, G., ii, 842.
Schumann, T. See R. F. Weinland.

Schuster, C. See F. Cornu.
Seidell, A., ii, 914.
Sellier, E., ii, 914.
Semmler, F. W., and A. Hoffmann, i, 946.
Senier, A., and A. Compton, Trans., 1927.
Seyewetz, A. See A. Lumière.
Shetterly, F. F. See A. W. Browne,
Sikorski, S. See D. Chardin.
Silvestri, S. See G. Bargellini.
Simon, L. J., and A. Conduché, i, 963.
Sjollema, B., and M. J. van't Kruys, ii, 907.
Slyke, D. D. Van. See L. L. Van Slyke.
Slyke, L. L. Van, and D. D. Van Slyke, i, 991.
Smith, A. R., and J. F. Thorpe, Trans., 1899.
Snell, J. F., ii, 869.
Sokoloff, W. See L. Tschugaeff.
Solodowinkoff, P. See A. Porai-Koschitz.
Spiegel, L., ii, 899.
Spiegler, E., i, 992.
Spring, W., ii, 860.
Stark, O., i, 973, 974.
Stenzel, G. See S. von Kostanecki,
Stern. See P. Pfeiffer.
Stern, M., and H. Thierfelder, ii, 896.
Stoermer, R., and D. Johannsen, i, 966.
Stull, W. N. See T. W. Richards.
Stutzer, A., ii, 906.
Sundwik, E. E., i, 887.
Széki, T. See R. Fabinyi.
Szilárd, B., ii, 888.

T.

Taber, W. See J. M. Bell.
Tafel, J., and J. Dodt, i, 984, 985.
Tafel, J., and P. A. Houseman, i, 984.
Tagliavini, A., ii, 913.
Tammann, G., ii, 857.
Tanatar, S., and E. Kurorski, i, 888.
Tebb, M. C. See O. Rosenheim.
Terres. See G. Just.
Thierfelder, H. See M. Stern.
Thomson, J. D. See H. G. Plimmer.
Thorpe, J. F. See A. R. Smith.
Tiffeneau, M., i, 922.
Tobler, A. See S. von Kostanecki.
Tollens, ii, 901.
Tombrock, W. See E. Cohen.
Tonegutti, M., ii, 908.
Travers, M. W., ii, 865.
Trieschmann, A. See P. Pfeiffer.
Troitzki, M. See A. Porai-Koschitz.
Truchsäss, H. See C. Liebermann.
Tschugaeff, L., i, 904.
Tschugaeff, L., and W. Sokoloff, i, 896.
Tsvett, M., i, 948.
Tucker, S. A., ii, 842.
Tutin, F. See M. Barrowcliff.

U.

Udby, O. See H. Goldschmidt.
Utz, F., ii, 916.

V.

Vandevelde, A. J. J., ii, 890.
Vegesack, A. von. See R. Sahmen.
Verdier. See Evesque.
Vetter, E. See E. Fromm.
Vieweg, W., i, 893.
Ville, J., ii, 913.
Voegtlin, C. See E. Abderhalden.
Vogt, W. See A. Windaus.

W.

Waal, J. W. de, i, 893.
Waentig, R. See L. Knorr.
Waidner, C. W., and G. K. Burgess, ii, 882.
Walker, J., and H. H. Beveridge, Trans., 1797.
Walker, W. H., A. M. Cederholm, and L. N. Bent, ii, 875.
Wallach, O., and A. Blumann, i, 936.
Wallach, O, F. Boedecker, and F. Meister, i, 943
Watson, J. A. See H. E. Armstrong.
Wechsler, E. See A. Lapworth.
Wedekind, E., ii, 874.
Wedekind, R., i, 942, 943.
Weehuizen, F., ii, 905.
Weibull, M., ii, 888.
Weigert, F., ii, 835, 838.
Weinland, R. F., and T. Schumann, ii, 877.
Westdeutsche Thomasphosphatwerke, ii, 863.
Weyl, T,, i, 907.
Wheeler, H. L., i, 929, 972.
Whymper, R., ii, 849.
Wick, F. G., ii, 834, 835.
Wiggers, C. J., ii, 901.
Wilke, E. See G. Bredig.
Williams, O. T., ii, 900.
Willstätter, R., and W. Heubner, i, 959.

Willstätter, R., and T. Kametaka, i, 936.
Wilsmore, N. T. M., Trans., 1938.
Windaus, A., and A. Hauth, i, 921.
Windaus, A., and W. Vogt, i, 978.
Winkelmann, A., ii, 846.
Winogradoff, N. See A. D. Bogojawlensky.
Winther, C., ii, 831, 832.
Wislicenus, W., and E. Breit, i, 967.
Wislicenus, W., and H. W. Bywaters, i, 968.
Woods, S. H. See B. E. Curry.
Wootton, W. O., Trans., 1890.

Z.

Zak, E., i, 996.
Zaleski, W., ii, 904.
Zaloziecki, R., and J. Hausmann. ii, 883.
Zanetti, J. E. See C. L. Jackson.

ERRATA.

Vol. XCI (Trans., 1907).

Page	Line	
1662	4*	*for* "$C_{13}H_{19}NClBr_2$" *read* "$C_{19}H_{12}NClBr_2$."

Vol. LXXXVI (Abstr., 1904).

Part I.

373	22	*for* "parasaccharic" *read* "parasaccharinic."
	23	,, "saccharic" *read* "saccharinic."
	25	,, "*metasaccharate*" *read* "*metasaccharinate.*"
	21*	,, "*parasaccharate*" ,, "*parasaccharinate.*"
	19*	,, "*saccharate*" *read* "*saccharinate.*"
	19*	,, "iso*saccharate*" *read* "iso*saccharinate.*"

---

* From bottom.

kindred substances; but our ignorance is correspondingly great of most of the blood colouring matters as well as of many coloured constituents of our own bodies: of the hair, the skin and the eye. The fullest recognition must be accorded, however, to recent investigations on the complex colouring matters of the blood and of chlorophyll, which is distantly related to the former, associated with the names of Schunck, Nencki, Marchlewski, Küster and Willstätter.

In fine, the aid of synthetical chemistry is required in every direction in arriving at a clear understanding of structure and of change. The methods at our disposal in the laboratory are doubtless altogether different from those which come into operation in the living world but chemists are already trying to effect changes in carbon compounds by means of so-called mild interactions, under conditions comparable with those which prevail in the living organism. It may suffice to refer to the development of a number of catalytic processes and to the comprehensive studies on the action of light on organic substances undertaken by Ciamician. In fact, the effort is already being made to co-operate with biology; it is clear that a section of the forces of organic chemistry is being directed once more towards the goal from which it set out. The separation from biology was necessary during the past century while experimental methods and theories were being elaborated; now that our science is provided with a powerful armoury of analytical and synthetical weapons, chemists can once more renew the alliance both to its own honour and to the advantage of biology. Indeed, the prospect of obtaining a clearer insight into the wondrous series of processes which constitute animal and vegetable life may well lead the two sciences to work with definite purpose to a common end.

In order, as far as possible, to avoid mistakes in this difficult task and to shield ourselves from the disappointment which is the inevitable consequence of exaggerated hopes, we cannot do better than strive to imitate the great example of Faraday, who always, with rare acumen, directed his attention to actual phenomena without allowing himself to be influenced by preconceived opinion, and who in his theoretical conceptions gave expression only to observed facts.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

CLXXXIX.—Aromatic Azoimides. Part III. The Naphthylazoimides and their Nitro-Derivatives. By **Martin Onslow Forster** and **Hans Eduard Fierz** 1942

CXC.—The Action of Phosphorus Pentachloride on Hydroxytrimethylsuccinic Ester. 1 : 2-Dimethyl*cyclo*propane-1 : 2-dicarboxylic Acid (1 : 2-Dimethyltrimethylene-1 : 2-dicarboxylic Acid). By **Herbert Henstock** and **Bertha Elizabeth Woolley** 1954

CXCI.—The Vapour Pressures of Triethylamine, of 2 : 4 : 6-Trimethylpyridine, and of their Mixtures with Water. By **Robert Tabor Lattey** 1959

CXCII.—Liquid Triethylamine. By **Robert Tabor Lattey** . 1971

CXCIII.—The Alcohols of the Hydroaromatic and Terpene Series. Part I. Resolution of the Alcohols into their Optically Active Components and the Preparation of the Borneols. By **Robert Howson Pickard** and **William Oswald Littlebury** 1973

CXCIV.—The Interaction of Metallic Sulphates and Caustic Alkalis. By **Spencer Umfreville Pickering**, M.A., F.R.S. 1981

CXCV.—The Chemistry of Bordeaux Mixture. By **Spencer Umfreville Pickering**, M.A., F.R.S. 1988

CXCVI.—Emulsions. By **Spencer Umfreville Pickering**, M.A., F.R.S. 2001

CXCVII.—The Electrolytic Preparation of Disulphides. Part I. Dibenzyl Disulphide and Diethyl Disulphide. By **Thomas Slater Price** and **Douglas Frank Twiss** 2021

PAGE

CXCVIII.—The Double Nitrites of Mercury and the Alkali Metals. By **Prafulla Chandra Rây** 2031

CXCIX.—Silver-mercuroso-mercuric Oxynitrates and the Isomorphous Replacement of Univalent Mercury by Silver. By **Prafulla Chandra Rây** 2033

CC.—The Constituents of the Essential Oil of Nutmeg. By **Frederick Belding Power** and **Arthur Henry Salway** . 2037

CCI.—The Resolution of *sec.*-Octyl Alcohol [Methylhexylcarbinol. Octane-2-ol]. By **Robert Howson Pickard** and **Joseph Kenyon** 2058

CCII.—The Alkyl Compounds of Gold. By **William Jackson Pope** and **Charles Stanley Gibson** 2061

CCIII.—Methyl Ethers of some Hydroxyanthraquinones. By **Arthur George Perkin** 2066

CCIV.—The Colouring Matters of the Stilbene Group. Part IV. The Action of Caustic Alkalis on para-Nitrotoluene and its Derivatives. By **Arthur George Green**, **Arthur Hugh Davies**, and **Ronald Smith Horsfall**. 2076

CCV.—The Replacement of Alkyl Radicles by Methyl in Substituted Ammonium Compounds. By **Humphrey Owen Jones** and **John Robertshaw Hill** 2083

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS.

A.

Abderhalden, E., and C. Funk, i, 1095.
Abney, Sir W. de W. See Sir H. E. Roscoe.
Ach, L., and H. Steinbock, i, 1069.
Adeney, W. E. See Sir H. E. Roscoe.
Aktien-Gesellschaft für Anilinfabrikation, i, 1049, 1076, 1081.
Allers, R. A., and S. Bondi, ii, 973.
Ammann, L. See L. Lindet.
Andrlík, K., V. Staněk, and J. Urban, ii, 984.
Armit, H. W., ii, 981.
Armstrong, H. E., J. J. Dobbie, M. O. Forster, A. Lapworth, T. M. Lowry, and S. Young, ii, 941.
Arnold, H. R. See J. Houben.
Arzalier, L. See W. Oechsner de Coninck.
Ascher, E. See C. Neuberg.
Atenstadt, P. See A. Beythien.
Auger, V., ii, 948.
Auwers, K., and O. Mahler, i, 1033.

B.

Badische Anilin- und Soda-Fabrik, i, 1024, 1085.
Bartal, A. von, ii, 957.
Bartelt, K. See F. W. Semmler.
Bartholdy, P. M., i, 1043.
Bauer, F., i, 1098.
Baumhauer, H., ii, 917.
Baur, E. See W. Kerp.
Beckmann, E., and F. Junker, ii, 927.
Bellucci, I., and F. Carnevali, ii, 960.
Benedicenti, A., ii, 980.
Berl, E. See G. Lunge.
Beyer, A. See H. Lee.
Beythien, A., and P. Atenstadt, ii, 992.
Bigelow, S. L., and A. Gemberling, ii, 933.
Bimbi, F. See A. Mazzucchelli.
Bistrzycki, A., and L. Mauron, i, 1039, 1045.
Blackman, P., ii, 931.
Blanc, G., i, 1058.
Bloch, L., ii, 944.
Bollenbach, H. F. See T. Curtius.
Bondi, S., i, 1014.
Bondi, S. See also R. A. Allers.
Bordas, F., ii, 956.
Bottazzi, F., ii, 979.
Bousfield, W. R., and T. M. Lowry, ii, 930.
Bradbury, R. H., ii, 939.
Brahn, B. See C. Neuberg.
Brasch, W., ii, 975.
Braun, J. von, i, 997.
Bredig, G., ii, 943.
Bredig, G., W. Fraenkel, and P. F. Ripley, ii, 941.
Brochet, A., ii, 965.
Broniewski, W. See A. N. Guntz.
Brown, P. E. See J. G. Lipman.
Brown, W., ii, 957.
Bruce, J. See R. Willstätter.
Brunck, O., ii, 989.
Bruner, L., and S. Tolloczko, ii, 935.
Bülow, C., and R. Weidlich, i, 1039.
Busch, M., and R. Hobein, i, 1075.
Buxton, B. H. See O. Teague.

C.

Cady, H. P., and D. F. McFarland, ii, 949.
Cahen, E. See G. T. Morgan.

Caldwell, R. J., i, 1012.
Cambi, L., ii, 960.
Campbell, F. H., ii, 968.
Campbell, N., ii, 943.
Cannon, W. B., ii, 974.
Carlson, T., i, 1001.
Carlson, T. See also P. Klason.
Carnevali, F. See I. Bellucci.
Chéneveau, C., ii, 920.
Chesneau, G., ii, 985
Chō, S. See R. Majima.
Clarke, F. W., ii, 972.
Clemm, H. See T. Curtius.
Coehn, A., and C. L. Jacobsen, ii, 926.
Cohen, L. See G. B. Frankforter.
Colombano, A., i, 1091.
Comanducci, E., i, 1068.
Coppock, J. B., i, 1009.
Cormimbœuf, H., ii, 994.
Craw, J. A., and G. Dean, ii, 982.
Cronheim, W., ii, 985.
Crossley, A. W. See E. Divers.
Crowther, J. A., ii, 922.
Curtius, T., H. F. Bollenbach, and H. Clemm, i, 1078.
Curtius, T., and A. Hoesch, i, 1079.
Czyhlarz, E. von, and O. von Fürth, i, 1101.

D.

Dakin, H. D., i, 1099.
Dakin, H. D., and M. D. Herter, i, 1035.
Danilewsky, B., ii, 981
Daufresne. See M. Tiffeneau.
Davies, A. H. See A. G. Green.
Dean, G. See J. A. Craw.
Decker, H., F. Dinner, T. von Fellenberg, E. Ferrario, L. Stern, and A. Würsch, i, 1064.
Delacre, M., i, 999.
Demjanoff, N. J., i, 1023.
Demjanoff, N. J., and K. Fortunatoff, i, 1032.
Denigès, G., ii, 993.
Denis, W., i, 997.
Dennstedt, M., ii, 986.
Densdorff, O. See E. Vongerichten.
Deutsch, E., i, 1082.
Deutsche Sprengstoff Aktien Gesellschaft, i, 998.
Dewar, Sir J. See Sir H. E. Roscoe.
Diels, O., and E. Sasse, i, 1086.
Diels, O., and E. Stephan, i, 1000.
Dimroth, O., and M. Hartmann, i, 1090.
Dinner, F. See H. Decker.
Divers, E., A. W. Crossley, M. O. Forster, W. H. Perkin, jun., and H. R. Le Sueur, i, 1018.
Dobbie, J. J. See H. E. Armstrong.
Donath, H., ii, 975.
Dony-Hénault, O., and Mlle. J. Van Duuren, i, 1100.
Doran, J. See E. P. Harding.
Duboin, A., ii, 955.
Dubsky, J. See A. Werner.
Duda, L. See K. Krassusky.
Dufour, A., ii, 920.
Dunstan, W. R., and T. A. Henry, i, 1063; ii, 983.
Duuren, Mlle. J. Van. See O. Dony-Hénault.

E.

Ebaugh, W. C., and C. B. Sprague, ii, 985.
Ebler, E., ii, 923.
Ehrenfeld, R., ii, 949.
Euler, H., i, 1098.
Evans, E. See O. Wallach.

F.

Fahr, G., ii, 978.
Falk, K. G., ii, 946.
Farbenfabriken vorm. Friedr. Bayer & Co., i, 1002, 1003, 1006, 1045, 1049, 1057, 1067, 1084, 1085.
Farbwerke vorm. Meister, Lucius, & Brüning, i, 1009, 1057, 1085, 1086, 1090.
Federlin, W., i, 1005.
Fellenberg, T. von. See H. Decker.
Fenyvessy, B. von. See L. von Liebermann.
Ferentzy, J. von, ii, 991.
Fernbach, A., and J. Wolff, i, 1012.
Ferrario, E. See H. Decker.
Fichter, F., J. Fröhlich, and M. Jalon, i, 1030.
Fierz, H. E. See M. O. Forster.
Filehne, W., i, 1035.
Fischer, E., and W. Schoeller, i, 1037.
Fischer, M. H., and G. Moore, i, 1095.
Forcrand, R. de, ii, 928.
Fornaini, M. See N. Parravano.
Forster, M. O., and H. E. Fierz, TRANS., 1942.
Forster, M. O. See also H. E. Armstrong and E. Divers.

Fortunatoff. K. See N. J. Demjanoff.
Fraenkel, A., ii, 973.
Fraenkel, W. See G. Bredig.
Franck, W. See H. Kauffmann.
Frankforter, G. B., and L. Cohen, ii, 988.
Franklin, E. C., and C. A. Kraus, ii, 929.
Freundlich, H., ii, 939.
Friedemann, F. See P. Klason.
Friedrich, K., ii, 951.
Fröhlich, J. See F. Fichter.
Fürth, O. von. See E. von Czyhlarz.
Fürth, O. von, and J. Schütz, ii, 976.
Funk, C. See E. Abderhalden.

G.

Gabriel, S., i, 1042.
Gailhat, J., ii, 986.
Gansser, E. See G. Hüfner.
Garcia, A., ii, 994.
Gaubert, P., ii, 939.
Geibel, W. See W. C. Heraeus.
Gemberling, A. See S. L. Bigelow.
Gerber, C., i, 1100.
Gialdini, C., i, 1005.
Gibbs, W. See Sir H. E. Roscoe.
Gibson, C. S. See W. J. Pope.
Gibson, W. H., and C. M. W. Grieb, ii, 985.
Gies, W. J. See M. Steel.
Ginsberg, W., ii, 980.
Glassner, F., and W. Suida, ii, 932.
Glover, W. H. See A. Hantzsch.
Goldberg, I., i, 1027.
Gonnermann, M., ii, 976.
Gontermann, W., ii, 968.
Goodwin, H. M., and R. D. Mailey, ii, 931.
Gorke, H. See H. Ley.
Graf, H. See O. Ruff.
Grandmougin, E., and J. R. Guisan, i, 1092.
Green, A. G., A. H. Davies, and R. S. Horsfall, Trans., 2076.
Gréhant, N., ii, 990.
Greshoff, M., ii, 983.
Grieb, C. M. W. See W. H. Gibson.
Guareschi, I., i, 1003.
Guisan, J. R. See E. Grandmougin.
Guntz, A. N., and W. Broniewski, ii, 948.
Guthzeit, M., and E. Hartmann, i, 1007.
Gutmann, P. See O. Wallach.

H.

Hahn, O., ii, 921.
Hantzsch, A., and W. H. Glover, i, 1055.
Hantzsch, A., and J. Oechslin, i, 1009.
Harding, E. P., and J. Doran, ii, 987.
Hardy, J. See J. Tarbouriech.
Harkort, H., ii, 959.
Hartley, W. N., ii, 917, 919.
Hartley, W. N. See also Sir H. E. Roscoe.
Hartmann, E. See M. Guthzeit.
Hartmann, M. See O. Dimroth.
Hauenstein, L. See G. Schultz.
Hauser, O., ii, 968.
Heffter, A., ii, 978.
Hell, C., and O. Schaal, i, 1049.
Henry, L., i, 1002.
Henry, T. A. See W. R. Dunstan.
Henstock, H., and Miss B. E. Woolley, Trans., 1954.
Heraeus, W. C., and W. Geibel, ii, 969.
Herlitzka, A., i, 1102.
Herter, M. D. See H. D. Dakin.
Herzog, R. O., ii, 939.
Herzog, R. O., and H. Kasarnowski, ii, 934.
Heusner, K. See C. Willgerodt.
Hewitt, J. T. See F. S. Kipping.
Hibbert, H. See A. Michael.
Hill, A. E. See M. A. Rosanoff.
Hill, J. R. See H. O. Jones.
Hindrichs, G., ii, 953.
Hinrichs, G. D., ii, 945.
Hissink, D. J., ii, 984.
Hobein, R. See M. Busch.
Hoering, P., i, 1017.
Hoesch, A. See T. Curtius.
Horsfall, R. S. See A. G. Green.
Houben, J., and H. R. Arnold, i, 1000.
Howe, P. E. See A. T. Lincoln.
Hüfner, G., and E. Gansser, i, 1097.
Hudson, C. S., ii, 942.
Hunter, W. H. See H. A. Torrey.

I.

Impens, E., ii, 977.

J.

Jacobsen, C. L. See A. Coehn.
Jaeger, F. M., i, 1050; ii, 923, 970.

Jalon, M, See F. Fichter.
Jamieson, G. S., ii, 951.
Jantsch, G. See A. Werner.
Jeriomin, K., ii, 954.
Johns, C. O. See H. L. Wheeler.
Johnson, T. B., and C. F. Speh, i, 1083.
Jones, H. O., and J. R. Hill, Trans., 2063.
Jorissen, A., i, 1063.
Jürgens, V., i, 1036.
Junker, F. See E. Beckmann.

K.

Kainoshô, T. See M. Kuhara.
Kalle & Co., i, 1008, 1073, 1090.
Kasarnowski, H. See R. O. Herzog.
Kauffmann, H., and W. Franck, i, 1092.
Kaufler, F., ii, 924.
Kazay, E. von, ii, 919.
Kehrmann, F., i, 1087.
Kenyon, J. See R. H. Pickard.
Kerp, W., and E. Baur, i, 1010, 1012; ii, 925.
Kiesel, A., ii, 994.
Kiliáni, H., and A. Sautermeister, i, 1011.
Kipping, F. S., J. T. Hewitt, A. Lapworth, K. J. P. Orton, and S. Ruhemann, i, 1027.
Klason, P., and T. Carlson, i, 1000.
Klason, P., F. Friedemann, and J. Köhler, i, 1029.
Klason, P., and E. Norlin, ii, 990.
Kleeman, R. D., ii, 923.
Klein, D. See A. T. Lincoln.
Knoll & Co., i, 1017, 1069, 1070.
Kobert, R., i, 1084.
Köhler, J. See P. Klason.
Königsberger, J. See W. J. Müller.
Kohler, E. P., i, 1050.
Krassusky, K., i, 999.
Krassusky, K., and L. Duda, i, 1013.
Kraus, C. A., ii, 935.
Kraus, C. A. See also E. C. Franklin.
Kuhara, M., and T. Kainoshô, i, 1027.
Kuhara, M., and M. Matsui, i, 1015.

L.

Lacroix, A., and A. B. de Schulten, ii, 971.
Langlet, A., ii, 955.
Lapworth, A. See H. E. Armstrong and F. S. Kipping.
Lasserre, A., ii, 991.
Lattey, R. T., Trans., 1959, 1971.
Lautsch, and G. Tammann, ii, 959.
Lee, H., and A. Beyer, ii, 927.
Leiser, H., ii, 967.
Leonard, A. G. G. See J. H. Pollok.
Le Sueur, H. R. See E. Divers.
Levin, M., ii, 922.
Lewis, H. F., ii, 925.
Lewkowitsch, J., and H. Pick, i, 997.
Ley, H., and H. Gorke, ii, 920.
Liebermann, L. von., B. von Fenyvessy, and P. von Liebermann, ii, 973.
Liebermann, P. von. See L. von Liebermann.
Liebig, H. von, i, 1045.
Lincoln, A. T., P. E. Howe, and D. Klein, ii, 953.
Lindet, L., and L. Ammann, i, 1095.
Linke, G. L. See A. Michaelis.
Lipman, J. G., and P. E. Brown, ii, 982.
Littlebury, W. O. See R. H. Pickard.
Liveing, G. D. See Sir H. E. Roscoe.
Lockyer, Sir W. N. See Sir H. E. Roscoe.
Lorenz, R., ii, 927.
Lovelace, B. F. See J. B. Tingle.
Lowry, T. M., ii, 928.
Lowry, T. M. See also H. E. Armstrong and W. R. Bousfield.
Lüppo-Cramer, i, 1098.
Lukens, H. S., and E. F. Smith, ii, 988.
Lumière, A., L. Lumière, and A. Seyewetz, ii, 921.
Lumière, L. See A. Lumière.
Lundberg, J., ii, 967.
Lundén, H., ii, 938.
Lunge, G., and E. Berl, ii, 948.

M.

McCutcheon, jun., T. P., ii, 988.
McCutcheon, jun., T. P., and E. F. Smith, ii, 988.
McFarland, D. F. See H. P. Cady.
Macnider, W. de B., and S. A. Matthews, ii, 981.
McPhail Smith, G., ii, 951.
Magnus-Levy, A., ii, 977, 979.
Magri, G., ii, 971.
Mahler, O. See K. Auwers.
Mailey, R. D. See H. M. Goodwin.
Majima, R., and S. Chô, i, 1032.
Malden, W., ii, 981.

Manwaring, W. H., ii, 973.
Marshall, W. E., ii, 995.
Mascarelli, L., i, 1021.
Mascarelli, L., and U. Pestalozza, ii, 936.
Matignon, C., ii, 957.
Matsui, M. See M. Kuhara.
Matthes, H., and F. Streitberger, ii, 991.
Matthews, S. A. See W. de B. Macnider.
Mauron, L. See A. Bistrzycki.
Maxwell, S. S., ii, 977.
Mayer, O., ii, 996.
Mazzucchelli, A., and F. Bimbi, i, 1004.
Merck, E., i, 1071, 1072, 1088.
Messerschmitt, J., ii, 918.
Meunier, J., ii, 989.
Meyer, G. M. See W. Salant.
Mezger, R. See J. Schmidt.
Michael, A., and H. Hibbert, i, 1010.
Michaelis, A., and G. L. Linke, i, 1102.
Michaelis, L., L. Pincussohn, and P. Rona, i, 1095.
Michaelis, L. See also P. Rona.
Milazzo, A. See A. Tamburello.
Molinari, E., i, 1039.
Monimart, R., ii, 993.
Moore, G. See M. H. Fischer.
Morgan, G. T., and E. Cahen, i, 1021.
Mori, Y., ii, 937.
Moscati, G., ii, 979.
Moser, L., ii, 988.
Müller, W. J., and J. Königsberger, ii, 924.

N.

Nägeli, W. See C. Willgerodt.
Neuberg, C., i, 997.
Neuberg, C., and E. Ascher, i, 1008, 1014.
Neuberg, C., and B. Brahn, i, 1097.
Neuberg, C., and E. Rosenberg, i, 1029.
Niementowski, S. von, i, 1081.
Noguchi, H., ii, 974.
Norlin, E. See P. Klason.
Norris, J. F., i, 1034.

O.

Oechslen, R. See E. Wedekind.
Oechslin, J. See A. Hantzsch.
Oechsner de Coninck, W., i, 1042.
Oechsner de Coninck, W., and L. Arzalier, ii, 952.
Orloff, E. I. i, 1008.
Orloff, N. A., ii, 955, 970.
Orton, K. J. P. See F. S. Kipping.
Osaka, Y., ii, 934.
Osaka, Y., and J. Yamasaki, ii, 941.
Osann, W. See P. Pfeiffer.
Ostwald, W., ii, 939, 976, 981.

P.

Palazzo, F. C. See A. Peratoner.
Pantanelli, E., ii, 983.
Parnas, J. See R. Willstätter,
Parr, S. W., ii, 928.
Parravano, N., and M. Fornaini, ii, 951.
Pellat, H., ii, 943.
Pellini, G., ii, 954.
Peratoner, A., and F. C. Palazzo, i, 1018.
Perkin, A. G., Trans., 2066.
Perkin, F. M., ii, 952.
Perkin, W. H., jun. See E. Divers.
Pestalozza, U. See L. Mascarelli.
Peteny, A. See G. Schultz.
Peters, W., ii, 944.
Pfeiffer, P., ii, 937.
Pfeiffer, P., and W. Osann, i, 1073.
Pfeiffer, P., and M. Tilgner, i, 1017.
Phelps, I. K., and M. A. Phelps, i, 1016.
Phelps, M. A. See I. K. Phelps.
Philip, J. C., ii, 935.
Pick, H. See J. Lewkowitsch.
Pickard, R. H., and J. Kenyon, Trans., 2058.
Pickard, R. H., and W. O. Littlebury, Trans., 1973.
Pickering, S. U., Trans., 1981, 1988, 2001.
Pickles, S. S., i, 1063.
Pincussohn, L. See L. Michaelis.
Pollok, J. H., ii, 917.
Pollok, J. H., and A. G. G. Leonard, ii, 918.
Pope, W. J., and C. S. Gibson, Trans., 2061.
Power, F. B., and A. H. Salway, Trans., 2037.
Prandi, O., ii, 946.
Price, T. S., and D. F. Twiss, Trans., 2021.
Purvis, J. E., ii, 919.

R.

Rakowsky, A. V., ii, 987.
Ranken, C., and W. W. Taylor, ii, 921.
Rapp, ii, 982.
Rasch, E., ii, 947.

Rây, P. C., Trans., 2031, 2033.
Redgrove, H. S., ii, 929.
Reiff, H. J., ii, 927.
Reis, R. See L. Rosenthaler.
Reissert, A., i, 1046, 1103.
Repiton, F., ii, 990.
Ripley, P. F. See G. Bredig.
Robertson, T. B., i, 1096.
Robin, L., ii, 993.
Robinson, H. H., i, 1012.
Roemer, H. See A. Thiel.
Rohland, P., ii, 957.
Romburgh, P. van, i, 1011.
Rona, P., and L. Michaelis, i, 1094.
Rona, P. See also L. Michaelis.
Rosanoff, M. A., and A. E. Hill, ii, 984.
Roscoe, Sir H. E., Sir W. de W. Abney, W. E. Adeney, Sir J. Dewar, W. Gibbs, W. N. Hartley, G. D. Liveing, Sir W. N. Lockyer, A. Schuster, and M. Watts, ii, 918.
Rosenberg, E. See C. Neuberg.
Rosenthaler, L., and R. Reis, i, 1009.
Rudorf, G., ii, 937.
Ruff, O., and H. Graf, ii, 947.
Ruhemann, S. See F. S. Kipping.
Rupe, H., and J. Splittgerber, i, 1016.
Ryn, W. van, ii, 995.

S.

Sachs, F., and W. Weigert, i, 1046, 1047, 1048.
Saiki, T., ii, 973.
Salant, W., ii, 976.
Salant, W., and G. M. Meyer, ii, 979.
Salomone, G., ii, 982.
Salway, A. H. See F. B. Power.
Sartory, A., ii, 982.
Sasse, E. See O. Diels.
Sautermeister, A. See H. Kiliáni.
Saxl, P., ii, 980.
Schaal, O. See C. Hell.
Schaller, W. T., ii, 971.
Scheiber, J., and H. Wolf, i, 1028.
Schmidt, F. W., i, 1014.
Schmidt, J., and R. Mezger, i, 1022.
Schmidt, J., and J. Söll, i, 1054.
Schmitt, C., i, 1007.
Schoeller, W. See E. Fischer,
Schütz, J. See O. von Fürth.
Schütz, E., ii, 947.
Schulten, A. B. de. See A. Lacroix.
Schultz, G., i, 1030.
Schultz, G., and L. Hauenstein, i, 1074.
Schultz, G., and A. Peteny, i, 1075.
Schuster, A. See Sir H. E. Roscoe.
Schwarz. See Valentiner.
Seidell, A., ii, 984.
Sella, A., ii, 934.
Semmler, F. W., and K. Bartelt, i, 1062.
Senter, G., ii, 935.
Seyewetz, A. See A. Lumière.
Sherry, R. H., ii, 920.
Shinn, F. L., ii, 926.
Shorygin, P., i, 1031.
Singh, P., ii, 994.
Skita, A., i, 1040.
Slyke, D. D. See L. L. Van Slyke.
Slyke, L. L. Van, and D. D. Van Slyke, i, 1096.
Smith, D. P., ii, 949.
Smith, E. F. See H. S. Lukens and T. P. McCutcheon, jun.
Soddy, F., ii, 944.
Söll, J. See J. Schmidt.
Soellner, J., ii, 972.
Sorger, C., i, 1041.
Speh, C. F. See T. B. Johnson.
Spiro, K., ii, 975.
Spitalsky, E., ii, 942.
Splittgerber, J. See H. Rupe.
Sprague, C. B. See W. C. Ebaugh.
Stadnikoff, G., i, 1015, 1016.
Stanëk, V. See K. Andrlík.
Steel, M., and W. J. Gies, i, 1097; ii, 975.
Steele, B. D., ii, 925.
Steensma, F. A., ii, 995.
Steinbock, H. See L. Ach.
Stephan, E. See O. Diels.
Stern, L. See H. Decker.
Steudel, H., i, 1097.
Streitberger, F. See H. Matthes.
Stroman, A., ii, 917.
Suida, W. See F. Glassner.
Swart, S. P., ii, 934.
Sztankay, von, i, 1071.

T.

Tamburello, A., and A. Milazzo, i, 1088.
Tammann, G. See Lautsch and W. Treitschke.
Tanret, C., ii, 995.
Tarbouriech, J., and J. Hardy, i, 1035.
Taylor, W. W. See C. Ranken.
Teague, O., and B. H. Buxton, ii, 932, 933.
Thatcher, R. W., and H. R. Watkins, ii, 983.
Thiel, A., and H. Roemer, ii, 940.

Tiffeneau, M., and Daufresne, i, 1035.
Tilgner, M. See P. Pfeiffer.
Tingle, J. B., and B. F. Lovelace, i, 1044.
Tolloczko, S. See L. Bruner.
Torrey, H. A., and W. H. Hunter, i, 1030
Treitschke, W., and G. Tammann, ii, 958.
Trephilieff, H., i, 1063.
Tschitschibabin, A. E., i, 1022.
Tschugaeff, L., ii, 989.
Twiss, D. F. See T. S. Price.

U.

Urano, F., ii, 978.
Urbain, G., ii, 956.
Urban, J. See K. Andrlík,

V.

Valentiner, and Schwarz, i, 1021.
Vesterberg, A., ii, 938.
Vidal, R., i, 1020.
Vongerichten, E., and O. Densdorff, i, 1068.

W.

Walden, P., i, 1017.
Wallach, O., i, 1058.
Wallach, O., E. Evans, and P. Gutmann, i, 1061.
Watanabe, T., ii, 967.
Watkins, H. R. See R. W. Thatcher.
Watts, M. See Sir H. E. Roscoe.
Watts, O. P., ii, 953.
Weber, H., i, 1071.
Wedekind, E., ii, 922.
Wedekind, E., R. Oechslen, and O. Wedekind, i, 1073.
Wedekind, O. See E. Wedekind.
Weidlich, R. See C. Bülow.
Weigert, W. See F. Sachs.
Werner, A., ii, 945, 961, 962, 963, 964, 965, 969.
Werner, A., and J. Dubsky, ii, 966.
Werner, A., and G. Jantsch, i, 1012.
Wheeler, H. L., and C. O. Johns, i, 1083.
Wieland, H., i, 1076.
Wikander, E. H. See C. Willgerodt.
Willgerodt, C., and K. Heusner, i, 1026.
Willgerodt, C., and W. Nägeli, i, 1025.
Willgerodt, C., and E. H. Wikander, i, 1024.
Willstätter, R., and J. Bruce, i, 1018.
Willstätter, R., and J. Parnas, i, 1056.
Wolf, H. See J. Scheiber.
Wolff, J. See A. Fernbach.
Woolley, Miss B. E. See H. Henstock.
Würsch, A. See H. Decker.

Y.

Yamasaki, J., ii, 953.
Yamasaki, J. See also Y. Osaka.
Young, S. See H. E. Armstrong.

Z.

Zubkowskaia, N., ii, 940.

ERRATA.

VOL. LXXXVIII (ABSTR., 1905).

PART I.

Page	Line	
508	23	*for* "1904, ii, 42" *read* "1904, i, 480."
508	17*	,, "the" *read* "methyl."
508	17*	,, "*ethyl*" read "*αγ-dimethyl ββ-diethyl.*"
508	16*	,, "$C(CO_2Et)_2[CH(CN)\cdot CO_2Et]_2$" *read* "$C(CO_2Et)_2[CH(CN)\cdot CO_2Me]_2$."

VOL. XCI (TRANS., 1907).

Page	Line	
763		*transpose* Fig. 3 to page 767.
767		,, Fig. 2 ,, 763.
1591	2	for "7(10)-*amino*-1-*naphthacenequinone*" read "7(10)-*amino*-1-*hydroxynaphthacenequinone*."
1640	4*	,, "$C_{16}H_{12}O_4$" *read* "$C_{12}H_{12}O_4$."

VOL. XCII (ABSTR., 1907).

PART I.

Page	Line	
952	11	for "6-*hydroxy*-4-iso*propylflavone*" read "6-*methoxy*-4-iso*propylflavanone*."
952	12	,, "cumenol" *read* "cuminaldehyde."
952	25	
952	1*	
953	16	
957	23*	,, "**Dioxycodeine**" *read* "**Deoxycodeine.**"

---

* From bottom.

with pure acetanilide made in the usual way. Similarly, from *o*-toluidine, aceto-*o*-toluidide, melting at 110°, was produced, and, from anhydrous liquid ammonia, acetamide, melting at 79°. The substance reacted vigorously with bromine. On distilling off the excess of bromine and adding alcohol to the residue, there was a further evolution of heat, and the residue had the characteristic pungent smell of bromoacetic ester, indicating that bromoacetyl bromide had first been formed.

There can therefore be no doubt that the new substance is a *keten*, having the formula $CH_2\!:\!CO$, although, as distinguished from Staudinger's disubstituted ketens, it may also exist in the form $CH\!:\!C\cdot OH$.

Since all the above-mentioned reactions begin readily at the ordinary temperature, and are, in fact, accompanied by evolution of heat, keten seems likely to prove a useful acetylating agent. It has a special advantage over other acetylating agents in that no by-products are formed in the reaction.

Keten has a peculiar penetrating smell, which persists for many hours if the gas has been inhaled in any but small quantities, and it attacks the mucous membranes. It is colourless in both the liquid and gaseous states, and on freezing it forms a white solid. It does not appear to react with dry oxygen, but it combines rapidly with water, forming, for the most part, acetic acid. The aqueous solution, however, also gives the chief reactions for an aldehyde, so that glycollaldehyde may be formed in small quantity at the same time. It may be noted here that, if keten could be made to react with water in the isomeric form $CH\!:\!CO\cdot H$, there would be a possibility of building up from it compounds containing the group $\cdot CH(OH)\cdot CH(OH)\cdot$.

The tendency of keten to condense on standing to a brown liquid has been already referred to. In the gaseous state, at the ordinary temperature and pressure, the reaction is fairly slow, that is to say, it is possible, by working quickly, to obtain a fair measurement of the gas in a gas burette, and the rate is further diminished by dilution with an indifferent gas. But in the liquid state, under pressure, the change is rapid and much heat is evolved. Porous substances, such as glass-wool, also hasten the reaction. The condensation product has not yet been studied.

The research is being continued.

University College,
University of London.

Chem – AC

No. DXXXVIII.] [August, 1907

JOURNAL

OF

THE CHEMICAL SOCIETY

CONTAINING

PAPERS COMMUNICATED TO THE SOCIETY,

AND

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN OTHER JOURNALS

Vols. XCI & XCII.

Committee of Publication:

H. E. Armstrong, Ph.D., LL.D., F.R.S.
E. C. C. Baly.
Horace T. Brown, LL.D., F.R.S.
A. W. Crossley, D.Sc., Ph.D., F.R.S.
Wyndham R. Dunstan, M.A., F.R.S.
M. O. Forster, D.Sc., Ph.D., F.R.S.
R. Meldola, F.R.S.
G. T. Morgan, D.Sc.
Sir W. Ramsay, K.C.B., LL.D., F.R.S.
A. Scott, M.A., D.Sc., F.R.S.
W. A. Tilden, D.Sc., F.R.S
John Wade, D.Sc.

Editor:

J. C. Cain, D.Sc., Ph.D.

Sub-editor:

A. J. Greenaway.

Assistant Sub-editor:

C. H. Desch, D.Sc., Ph.D.

Abstractors:

E. F. Armstrong, Ph.D., D.Sc.
C. F. Baker, Ph.D., B.Sc.
W. A. Davis, B.Sc.
H. M. Dawson, Ph.D., B.Sc.
T. Ewan, B.Sc., Ph.D.
W. H. Glover, Ph.D.
E. Goulding, D.Sc.
P. Haas, D.Sc., Ph.D.
W. D. Halliburton, M.D., F.R.S.
T. A. Henry, D.Sc.
E. Horton, B.Sc.
L. M. Jones, B.Sc.
L. De Koningh.
Z. Kahan, B.Sc.
A. McKenzie, M.A., D.Sc.
N. H. J. Miller, Ph.D.
G. T. Morgan, D.Sc.
K. J. P. Orton, M.A., Ph.D.
J. C. Philip, M.A., Ph.D.
T. H. Pope, B.Sc.
W. Robertson.
G. Senter, Ph.D., B.Sc.
W. P. Skertchly.
C. Smith, D.Sc.
L. J. Spencer, M.A.
J. J. Sudborough, Ph.D., D.Sc.
A. Jamieson Walker, Ph.D., B.A.
E. W. Wheelwright, B.A., Ph.D.
M. A. Whiteley, D.Sc.
G. Young, Ph.D.

LONDON:
GURNEY AND JACKSON (Successors to J. Van Voorst)
10 PATERNOSTER ROW.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

3610

LIBRARY.

The Library is open for consultation and for the issue and return of books daily from 10 A.M. to 6 P.M. (Saturdays 10 A.M. to 2 P.M.), and in the evenings of those days on which the Chemical Society meets.

PUBLICATIONS OF THE SOCIETY.

With the exception of a few numbers of the Journals and Proceedings which are out of print, the following publications may be obtained from Messrs. Gurney and Jackson, 10, Paternoster Row, E.C.

		Price to Fellows.			Price to Public.		
		£	s.	d.	£	s.	d.
Memoirs and Proceedings, 1841—1847 (3 Vols.) ...	per vol.	1	0	0	1	10	0
Quarterly Journal, 1848—1862 (14 Vols.)	per vol.	1	0	0	1	10	0
,, ,, ,, ,, (Single Parts)	per part		5	0		7	6
Journal, 1862—1895	per vol.	1	10	0	1	10	0
,, ,, ,, (Single Parts)	per part		2	6		2	6
,, 1896 to present date	per vol.	2	0	0	2	0	0
,, ,, ,, (Single Parts)	per part		3	6		3	6
Proceedings, 1885 to present date	per vol.		7	6		7	6
,, ,, ,, (Single Parts) ...	per part			6			6
Annual Reports on the Progress of Chemistry (bound in cloth), Vols. I (1904), II (1905), III (1906)	per vol.		4	6		4	6
Collective Index, Vol. I. 1841—1872	per vol.		4	0		4	0
* ,, ,, ,, II. 1873—1882	per vol.		10	0		15	0
* ,, ,, ,, III. 1883—1892	per vol.		15	0	1	0	0
* ,, ,, ,, IV. 1893—1902	per vol.	1	0	0	1	10	0
†Jubilee Volume, 1891..			6	0		6	0
†Memorial Lectures, 1893—1900			7	6		7	6
†Library Catalogue, 1886			1	0		1	0
,, ,, 1903			2	6		2	6
†Cases for binding the Journal in 4 vols.	per year		4	0		4	0
Tables of International Atomic Weights (as recommended by the International Atomic Weights Committee). 1*s.* 6*d.* per dozen ; 12*s.* per hundred.							

* *Postage to Fellows One Shilling extra.*
† *Post free to Fellows.*

The Journal, which is published on the last day of each month, includes the Transactions of the Chemical Society and Abstracts of chemical papers published in other Journals.

The Proceedings contain certain papers read at the meetings and abstracts of the remainder and of the discussions. They are, as a rule, issued to the Fellows about a week after each Ordinary Meeting.

The Annual Reports on the Progress of Chemistry contain an epitome of the principal definite steps in advance which have been made during the year. Fellows can obtain, from the Assistant Secretary, cases for binding the Annual Reports, price One Shilling each.

Officers and Council.

Elected March 22, 1907.

PRESIDENT.

Sir WILLIAM RAMSAY, K.C.B., LL.D., F.R.S.

VICE-PRESIDENTS

WHO HAVE FILLED THE OFFICE OF PRESIDENT.

E. ARMSTRONG, Ph.D., LL.D., F.R.S.
CRUM BROWN, D.Sc., LL.D., F.R.S.
IR WILLIAM CROOKES, D.Sc., F.R.S.
IR JAMES DEWAR, M.A., LL.D., F.R.S.
G. VERNON HARCOURT, D.C.L., F.R.S.
APHAEL MELDOLA, F.R.S.
IUGO MÜLLER, Ph.D., LL.D., F.R.S.

W. ODLING, M.A., M.B., F.R.S.
Sir WILLIAM H. PERKIN, LL.D., F.R.S.
J. EMERSON REYNOLDS, Sc.D., F.R.S.
Sir HENRY E. ROSCOE, LL.D., F.R.S.
W. J. RUSSELL, Ph.D., F.R.S.
T. E. THORPE, C.B., LL.D., F.R.S.
W. A. TILDEN, D.Sc., F.R.S.

VICE-PRESIDENTS.

J. DOBBIE, M.A., D.Sc., F.R.S.
RUDOLPH MESSEL, Ph.D.
Sir ALEXANDER PEDLER, C.I.E., F.R.S.

W. H. PERKIN, Ph.D., F.R.S.
A. SMITHELLS, B.Sc., F.R.S.
W. P. WYNNE, D.Sc., F.R.S.

TREASURER.

ALEXANDER SCOTT, M.A., D.Sc., F.R.S.

SECRETARIES.

M. O. FORSTER, D.Sc., Ph.D., F.R.S.
A. W. CROSSLEY, D.Sc., Ph.D., F.R.S.

FOREIGN SECRETARY.

HORACE T. BROWN, LL.D., F.R.S.

OTHER MEMBERS OF THE COUNCIL.

E. C. C. BALY.
G. T. BEILBY, F.R.S.
BERNARD DYER, D.Sc.
W. R. E. HODGKINSON, Ph.D.
E. GRANT HOOPER.
H. A. D. JOWETT, D.Sc.

H. R. LE SUEUR, D.Sc.
F. E. MATTHEWS, Ph.D.
G. T. MOODY, D.Sc.
A. G. PERKIN, F.R.S.
W. J. SELL, M.A., D.Sc., F.R.S.
JOHN WADE, D.Sc.

ASSISTANT SECRETARY.

S. E. CARR.

LIBRARIAN.

F. W. CLIFFORD.

IMPORTANT NOTICES.

NOTICES TO AUTHORS OF PAPERS.

All communications for the Journal and for the Proceedings of the Society should be addressed to "The Secretaries, Chemical Society, Burlington House, W."

The attention of authors is directed to the following resolutions of the Council.

"No communication shall be included in the list of titles of papers to be brought before a Meeting of the Society, unless it is in the hands of the Secretaries **at least three days** before the date of the Meeting; and no announcement of titles can be made in the Proceedings until the communications have been received by the Secretaries."

"Papers which, on the report of referees, are deemed by the Council unsuitable for publication in the Transactions, shall be deposited in the Society's Archives." Authors are therefore advised to retain copies of their papers.

In all cases, an abstract of the paper, not exceeding three hundred words in length, should be supplied for insertion in the Proceedings. Communications are put down on the list for reading in the order in which they are received.

Authors are requested to write on their papers and abstracts the **address to which they wish proofs to be sent,** also to send their corrected proofs without delay to the **Editor, 28, Pembury Road, Clapton, N.E.,** *and not to the Printers.* If authors require more than the **50** copies allowed by the Society, they should inform the Editor at the time they send in their corrected proofs, when the extra copies will be supplied at cost price.

It has been resolved by the Council that communications made to the Society which have **already appeared in any Foreign Journal** shall not be published in the Society's Transactions, unless this course is **specially recommended** by the Publication Committee, and this recommendation approved by the Council.

ILLUSTRATIONS, AND PLATES OF CURVES.

As the **Illustrations** for the Journal (including curves) are, as far as possible, executed in photographic "process" work, the drawings, &c., accompanying the papers **must be drawn carefully on a scale about twice the size of the finished block, on smooth white Bristol board in Indian ink, so as to admit of the blocks being prepared directly from the drawings.** Any lettering on these drawings should be of such a size that it will be clearly legible when reduced.

When it is necessary to employ **Plates,** these must be also of convenient dimensions.

Information as to **Illustrations** and the dimensions of **Plates** can be obtained on application to the Editor.

Abstractors are requested to send their MSS. and corrected proofs to the **Sub-editor,** The Orchard, Chertsey, Surrey, and to communicate change of address to the **Printers** (Messrs. Richard Clay and Sons, Limited, 8, Bread Street Hill, E.C.), as well as to the **Editors.**

UN 17 1909

3 9015 06712 9281